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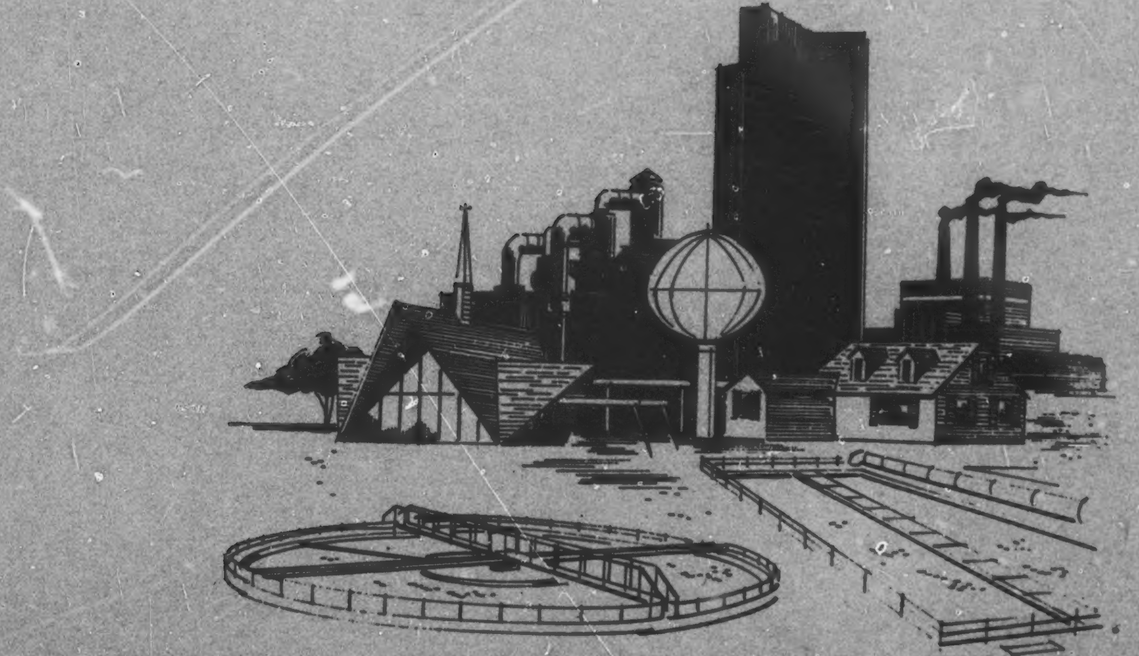
Magnesium Carbonate, A Recycled Coagulant for Water Treatment



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16. Abstract Laboratory investigations into the use of magnesium carbonate instead of alum for coagulation have demonstrated that the magnesium carbonate system produces a treated water with superior characteristics compared to water treated with alum. Both turbidity and organic color removals were comparable for both processes, and the flocs formed by the magnesium carbonate process were larger and heavier than alum flocs with better settling characteristics. The process involves the use of the magnesium carbonate as a coagulant and lime is added to precipitate gelatinous $Mg(OH)_2$. The sludge, composed of a slurry of $Mg(OH)_2$, $CaCO_3$, and clay is carbonated and the $Mg(OH)_2$ selectively and completely dissolved. Recycle after filtering allows re-use of both the magnesium carbonate and the sludgewater. $CaCO_3$ can also be recovered easily in large plants or landfilled at small ones. An optimal dosage relationship determined for 17 natural waters is: Optimum $MgCO_3 \cdot 3H_2O$ dosage (mg/l) = 8.33 + .03 (turbidity-mg/l) + 0.46 (organic color-mg/l) - .03 (total alkalinity-mg/l) + .14 (total hardness-mg/l). Chemical treatment costs for most waters can be substantially reduced using this system, while the quality of treated water will be superior to the quality of alum-treated water. (Lowry-Texas)

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MAGNESIUM CARBONATE, A RECYCLED COAGULANT FOR WATER TREATMENT

by

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June, 1971

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ABSTRACT

An entirely new system of water treatment has been developed. It is a unique combination of softening and conventional coagulation, and may be used for all types of waters, surface or ground, hard or soft. Magnesium carbonate is used as the coagulant and lime is added to precipitate gelatinous $Mg(OH)_2$, which is as effective as alum for the removal of both turbidity and organic color. The flocs formed are larger and heavier than alum floc, since they are "loaded" with $CaCO_3$. The sludge, composed of a slurry of $CaCO_3$, $Mg(OH)_2$ and clay is carbonated with CO_2 and the $Mg(HO)_2$ selectively and completely dissolved as the bicarbonate. The carbonated slurry is filtered and the filtrate recycled to the point of addition of chemicals to the raw water and reprecipitated with lime thus recovering both the coagulant and the sludge water. In small plants, the filter cake of $CaCO_3$ can be used as land fill. In larger plants, it is slurried in a flotation cell and the clay separated and used as land fill. The purified $CaCO_3$ is filtered and the cake passes to a multiple hearth furnace or Kiln and calcined to high quality lime. Chemical treatment costs are substantially reduced for most waters and the quality of the treated water is superior to that treated with alum.

This report was submitted in fulfillment of Water Quality Research Grant Project 12120 ESW with the Environmental Protection Agency.

Key Words: Water Purification, Coagulation, Chemical Precipitation, Sludge Treatment, Industrial Wastes.

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SECTION I. CONCLUSIONS

1) Magnesium carbonate, hydrolyzed with lime, is as effective as alum for the removal of both turbidity and organic color from surface waters. The flocs formed are larger and heavier than alum flocs and settle better.

2) An optimum dosage of magnesium hydroxide is required for acceptable treatment of each water. This requirement is related to the physical and chemical characteristics of the water, with organic color having the greatest effect. This relationship, determined for 17 natural waters, is:

   Optimum $MgCO_3 \cdot 3H_2O$ dosage (mg/1)
   = 8.33 + .03 (turbidity)
   + .46 (organic color) - .03 (total alkalinity)
   + .14 (total hardness).

   The coefficients for color and turbidity in the several natural waters used were in excellent agreement with the coefficient in the equations developed for synthetic waters.

3) Neither the base exchange capacity of the clay nor the level of turbidity present had a significant effect on the optimum coagulant dosage.

4) For each water studied, one specific flocculant was usually found superior to all others tested. In general, however, soft waters responded best to 0.5 ppm dosages of alum, whereas either activated silica or potato starch produced better flocs in hard waters.

5) The measurement of electrophoretic mobility is an effective analytical tool for evaluating coagulation efficiency, particularly in the coagulation of organic color. Charge reversal does not result in restabilization of the colloidal particles.

6) In the study with natural waters, considerably more magnesium was found in solution after coagulation than would have been predicted from theoretical magnesium hydroxide solubility data. This may have been due to the fact that true equilibrium was not reached in the relatively short settling periods allowed. A significant difference was found between values for residual magnesium determined by EDTA and those determined by atomic absorption spectrophotometry.

7) A series of graphs makes possible the determination of the optimum coagulation pH and the chemical treatment cost for lime, CO_2, and $MgCO_3$ based on jar test results. While the cost data are based on conservative estimates, significant savings in treatment costs are indicated for most waters without considering the many other benefits resulting from the use of this new treatment process.

8) Carbonation recovered nearly 100% of the magnesium hydroxide from the sludge with an insignificant amount of calcium solubilization. Release of coagulated color is not a problem where the average color in the water is less than 100. Filterability of the carbonated sludge will not be a problem for most waters. However, in the case of very soft waters the sludge will be low in $CaCO_3$ and it may be necessary to add a synthetic organic polyelectrolyte or an inert filter aid to provide satisfactory filterability.

9) The use of magnesium carbonate in most cases produces a treated water with superior chemical characteristics compared to water treated with alum. When magnesium is used, the treated waters have alkalinities ranging from 30 to 50 mg/l, giving soft waters sufficient alkalinity for calcium carbonate stabilization or softening waters high in carbonate hardness.

SECTION II. RECOMMENDATIONS

The problem of neglecting important research areas in new technological studies is discussed in the Introduction. While many new and exciting findings are reported as a result of this work, many more challenging areas of research have been exposed. For discussion purposes, these studies are divided into "applied" and "basic" research studies.

A two year research project should be initiated to implement this new process, first on pilot plant scale and later in a suitable municipal water plant. This study is required before this new process can be utilized in water plants throughout the country. The objectives of such a project would be to study or evaluate the following:

1) Operational procedures and problems in the use of this new process to treat a soft, colored, highly turbid river water subject to wide variations in chemical and physical characteristics.

2) Economic considerations of all cost involved in the use of this new process including projected capital expenditures for plant modifications.

3) Instrumentation and control of the carbonation and coagulant recycle processes.

4) Sludge filterability and the methods available for improvement. The effect of increasing hardness on sludge filterability will be studied by adjusting the raw water characteristics over a fairly wide range.

5) The effect of this new process on the future design of flocculation and settling basins. Laboratory observations indicate that less mixing and settling time is required as compared with alum treatment.

6) The benefits resulting from the increase in alkalinity and hardness resulting from the treatment of very soft water using magnesium carbonate. Comparison will be made of the corrosion or deposition potential of waters treated with magnesium carbonate and with alum.

7) Bacteriological removals in each unit to determine if prechlorination is required.

8) Iron and manganese removal to determine if the high pH is sufficient to precipitate the two metals completely.

Magnesium carbonate offers considerable promise in the treatment of municipal and industrial wastes. Magnesium forms a very insoluble complex, magnesium ammonium phosphate, which, when precipitated with $MgCO_3$ and lime, could provide tertiary sewage treatment at an acceptable cost. Simultaneously color, turbidity, and biological and chemical oxygen demand would be reduced to low and hopefully to satisfactory levels. Lime and magnesium values can be recovered and recycled as in water treatment, thus reducing the chemical costs. A research project to investigate this application has been begun at Gainesville, Fla.

Magnesium carbonate treatment of industrial wastes high in color such as the pulp and paper wastes, tannery wastes, textile dye wastes, etc. appears very attractive. More industrial plants have an unlimited supply of carbon dioxide in the stack gases and many already recover lime. A method of coagulant recycling for these highly colored wastes should be developed. This might be accomplished by the addition of a strong oxidant to the recycle stream after which the magnesium could be recovered by precipitation as magnesium carbonate tri-hydrate. The precipitated magnesium could be lightly calcined, 500-600°C, to burn off the organics and then reused.

The release of absorbed undesirable constituents by carbonation for coagulant recovery is in need of further study. For an industrial waste this might include heavy metals while the release of iron and manganese would be of concern in water treatment.

Basic research on the chemical interactions between magnesium and complexing ligands should be undertaken. Complexation, chelation, and ion pair formation should be studied. These mechanisms could possibly explain the lower magnesium values reported by EDTA titration as well as provide information as to how this problem can be eliminated. It is possible that the stability constants for some of these magnesium-ligand complexes are greater than that for the EDTA-magnesium complex under certain conditions. Possibly a strong oxidant will destroy these complexes, allowing an accurate titration of the magnesium by EDTA.

The identification of various magnesium species formed at high pH is an area for further research. Possibly polynuclear, strongly hydrated hydrolysis products form, as has been proposed for aluminum. Additional study of the effect of both anions and cations on the mobility of magnesium hydroxide flocs should be conducted.

The removal of tastes and odors is a serious problem faced by practically all municipal water treatment plants treating soft surface waters. The effect of the very high pH values used in coagulation with magnesium carbonate and lime on the removal of these tastes and odors by activated carbon and by other methods should be carefully studied.

SECTION III. INTRODUCTION

Iron and particularly aluminum salts have served well in the coagulation and clarification of water since their common usage in the early 1900's. Many investigators consider the highly hydrated and gelatinous property of the hydrolysis products to be a main attribute for their effectiveness. This property however makes dewatering and disposal of the sludge produced from the treatment process extremely difficult and costly. Water plant wastes are recognized today as an industry-wide pollution problem that must be solved. It is estimated that over 1,000,000 tons of alum sludge are produced each year with less than eight percent receiving treatment of any kind before disposal.[1]

The characteristics of the waste products from water plants are highly variable both within and among plants. A considerable effort has been made to characterize these wastes with the following ranges in characteristics being reported:[2,3,4]

Total Solids	1,000 - 17,000 mg/l
Suspended Solids	75% - 90% of Total Solids
Volatile Solids	20% - 35% of Total Solids
$BOD_{(5)}$ (Ultimate BOD considerably higher)	30 - 150 mg/l
COD (Higher value where activated carbon present)	500 - 15,000 mg/l

The reduction of volume and moisture content is of primary concern in alum sludge disposal. In a study of two water plants, Neubauer[2] found the volume of alum sludge produced to range from .12 to .26% of the total plant flow. Methods, which have been employed with varying degrees of success, to concentrate and dewater alum sludge include:

1) Gravity thickening, stirred thickeners, and lamella sedimentation[2,6,7]

2) Lagoons[2,3,5]

3) Drying beds[8]

4) Wedge wire filtration[9]

5) Vacuum filtration[6]

6) Pressure filtration[6]

7) Centrifugation[6]

8) Freezing[6]

As a means of offsetting some of the costs for treating the sludge, alum recovery has been attempted at several water plants. Jewell[10] in 1903 patented sulfuric acid regeneration of alum and in 1923 Mathis[11] obtained a similar patent. In 1951 Black Laboratories[12] suggested utilizing sulfur dioxide gas from boiler stacks as a source of sulfuric acid for alum recovery at Orlando, Florida. Roberts and Roddy[13] reported on investigations for alum recovery at Tampa, Florida which later was practiced for a short while but was discontinued due to operational problems. Tampa's source of raw water varied widely in hardness and organic color content. Aluminum sulfate was used only during times of high organic color making recovery an intermittent operation. Higher dosages of recovered alum had to be used due to the release from the sludge of organic color, reducing the effectiveness of the coagulant. The Asaka Purification Plant in Tokyo reports recovery of as much as 80% of the aluminum using the sulfuric acid process.[14] Iron or manganese, which might be present in the sludge, is also solubilized. This causes an increase in the concentration of these elements, making it necessary to waste a portion of the recovered alum from time to time.[15] Alum recovery is also practiced at the Daer Works in Scotland[6] and is being investigated for use at Minneapolis, Minnesota.[16]

Lime recovery in softening plants is practiced in several American cities with profitable operations being reported for two cities.[16,17] The excess lime produced is sold to neighboring cities for a profit. Lime recovery is presently economically attractive only for softening plants using 20 to 25 tons of lime a day.

While there are many methods of treating an alum sludge, only in unusual cases has the treatment been found to be satisfactory or economically attractive. The AWWA conference report on plant needs[16] states

> In summation, the principal needs are to find effective and economical means, through research, to dispose of water treatment plant wastes by direct treatment of sludge, or by eliminating undesirable chemicals, such as alum, through changes in water treatment methods.

In answer to these needs, an entirely new system of water treatment chemistry has been developed utilizing magnesium carbonate as the coagulant. The addition of sufficient lime slurry to a water containing magnesium bicarbonate and/or to which magnesium carbonate has been added, precipitates both magnesium hydroxide and calcium carbonate. Carbonation of the sludge solubilizes the magnesium, as magnesium bicarbonate, which can be recovered by vacuum filtration and the filtrate recycled and reused. The filter cake of $CaCO_3$ and clay is easily handled and disposed of as land fill. Lime recovery would further reduce the volume of sludge to be disposed of.

The flocculant properties of magnesium hydroxide have long been evident. It is these properties, however, which have troubled conventional water softening plants. The gelatinous nature of magnesium hydroxide, in many ways similar to the hydrolysis products of aluminum, makes the dewatering of the sludge difficult. Also, where recovery of lime is practiced, the magnesium hydroxide must be separated before calcination because of build-up of insoluble magnesium oxide in the recovered lime. Various techniques have been developed to separate the magnesium hydroxide from the calcium carbonate. The use of a centrifuge to selectively classify it into the centrate does not provide the degree of separation needed. Three-phase selective softening has been used at Lansing, Michigan for some years during the winter months of low water demand.[18] In the research activities herein described, the dosage of lime added in the first phase is just sufficient to precipitate the calcium bicarbonate and convert the magnesium bicarbonate to the soluble carbonate. In the second phase, excess lime is added to precipitate all magnesium hardness as $Mg(OH)_2$. This requires a lime dosage well above the stoichiometric amount. This second phase effluent with a pH of about 11.3 passes to the third phase where it is mixed with just enough raw water to utilize the excess lime in removing calcium hardness. Phases 1 and 3 sludges are mainly $CaCO_3$ - phase 2 sludge mainly $Mg(OH)_2$. Since this process cannot be used to soften waters containing either color or turbidity and requires extremely careful control, it is seldom used.

Bureau of Mines Technical Paper No. 684[19] describes an industrial process for separating MgO from its ores, brucite or dolomite, in which the calcined and finely ground ore is slurried and chilled. The MgO present is then dissolved by pure CO_2 with continuous cooling to neutralize the high heat of hydration of the MgO.

Black and Eidsness[20] were able to selectively dissolve the $Mg(OH)_2$ from the $CaCO_3$ in the lime-soda softening sludge at Dayton, Ohio, thus making it possible to recalcine the $CaCO_3$ and produce high quality quicklime. This sludge carbonation basin, the only one of its kind in the world, has been operating successfully since 1958.

While magnesium hydroxide was formerly regarded as a liability it has been recognized as an effective coagulant. Flentje,[21] in 1927, found increasing clarification efficiency in the water treatment plant at Oklahoma City as excess lime was added. He reasoned this to be due to precipitation of magnesium as the hydroxide. Several jar tests were performed which indicated that magnesium, in the form of magnesium chloride, is an effective coagulant. The excess lime treatment was practiced in conjunction with ferric sulfate on a full plant scale, to treat the hard, turbid river water. The objective was to employ the magnesium bicarbonate naturally present in the water. Flentje noted no decrease in filter runs, less algae in the settling basins, and greater bacteria removal. No attempt at coagulant recycle was made and the excess lime fed was not sufficient to quantitatively precipitate the magnesium present in the water.

In 1966, Lecompte[22] reported the use of magnesium carbonate as a coagulant for the reclamation of water within a paper mill. Lime was reacted with magnesium carbonate, produced by the reaction of finely ground magnesium oxide and bicarbonate alkalinity present in the water, to precipitate magnesium hydroxide. No attempt was made at magnesium recovery. The water to be treated contained 0.5 to 1.0 pounds of suspended solids per one thousand gallons with fluctuations in organic color. The chemical cost of the water produced was estimated at sixty-five dollars per million gallons with additional disinfection benefits noted due to the excess causticity.

Although water chemists have long recognized the effectiveness of magnesium hydroxide as a coagulant, the use of magnesium salts has not received acceptance for economic reasons. Both the chloride and the sulfate cost more per pound than alum and their use, in conjunction with lime, would increase the non-carbonate hardness of the water being treated in direct ratio to the make-up dosage required. The cost of magnesium carbonate currently quoted at 16¢ per pound, has always been prohibitive. However, three factors now indicate that the widespread use of magnesium carbonate should receive the most careful consideration:

1) As stated previously, treatment of water plant wastes is becoming mandatory. The dewatering of this sludge is an inherant benefit of the magnesium recovery process.

2) Recovery and recycle of a coagulant have not proven practical in the past. An economical, easily controlled process is not available for the recovery of magnesium carbonate for coagulant recycle.

3) A new low-cost source of magnesium carbonate will soon be available.[23] It will be recovered at low cost from the sludges produced by major plants softening high magnesium waters. Such plants will be able to substantially reduce their chemical treatment costs by (a) eliminating the use of alum, (b) sale of recovered magnesium carbonate and (c) recalcination, recycling and reuse of lime. Of perhaps equal importance is the fact that in so doing, they will have eliminated their individual sludge pollution problems.

For many waters, this new treatment method will result in considerable economic savings, and for all waters, it will solve the problem of sludge dewatering and disposal. As coagulation will take place generally in the pH range of 11.0 to 11.4, the need for prechlorination should be minimized and in many cases eliminated. Houston[24] and Hoover[25] were among the first investigators to report the effect of high pH on disinfection in water treatment. In 1952, Riehl _et al_.[26] reported that at a pH level of 11.0 to 11.5 and a contact time of four hours, the removal of bacterial organisms is on the order of 100%.

Alum and ferric sulfate have been shown to be effective in the coagulation of viruses.[27] However, these investigators found that viruses removed in the floc fraction were not destroyed and active virus can be recovered from the floc. Berg et al.[28] have found that disinfection of polio virus can be accomplished by high pH. Figure 1, from this publication, shows the effect of pH on the survival of polio virus as a function of time. It can be concluded that to some extent bacteria and virus can be removed by the new treatment process.

In this high pH range of coagulation, complete precipitation of iron and manganese should occur, possibly eliminating the need for more costly treatment methods. This pH environment would be unfavorable for aquatic growths in settling basins. The overall effect would be reduction in the use of chlorine and subsequent cost savings at the same time increasing the treatment efficiency.

In initial studies of new technology, important areas of research must be left for future investigations because of time limitations. The use and recycle of magnesium carbonate is an entirely new concept in water treatment chemistry. Initial research efforts have been planned to determine if this process is technically and economically feasible. The scope and objectives of this research were therefore as follows:

1) Evaluation of the parameters involved in the use and recycle of magnesium carbonate as a coagulant for both organic color and turbidity in soft waters. Studies of both synthetic and natural waters are included in this phase of the research.

2) Development of a predictive equation to determine the magnesium requirements based on the physical and chemical characteristics of a water.

3) Demonstration of the effectiveness of this new process on a broad spectrum of natural waters. Waters from the largest cities in the country were chosen to provide a wide spectrum of range in chemical and physical characteristics.

4) Estimation of the chemical cost of treatment using this new technology and comparison with the chemical costs using alum treatment.

5) Comparison of the chemical characteristics of the treated waters using magnesium carbonate and alum treatment.

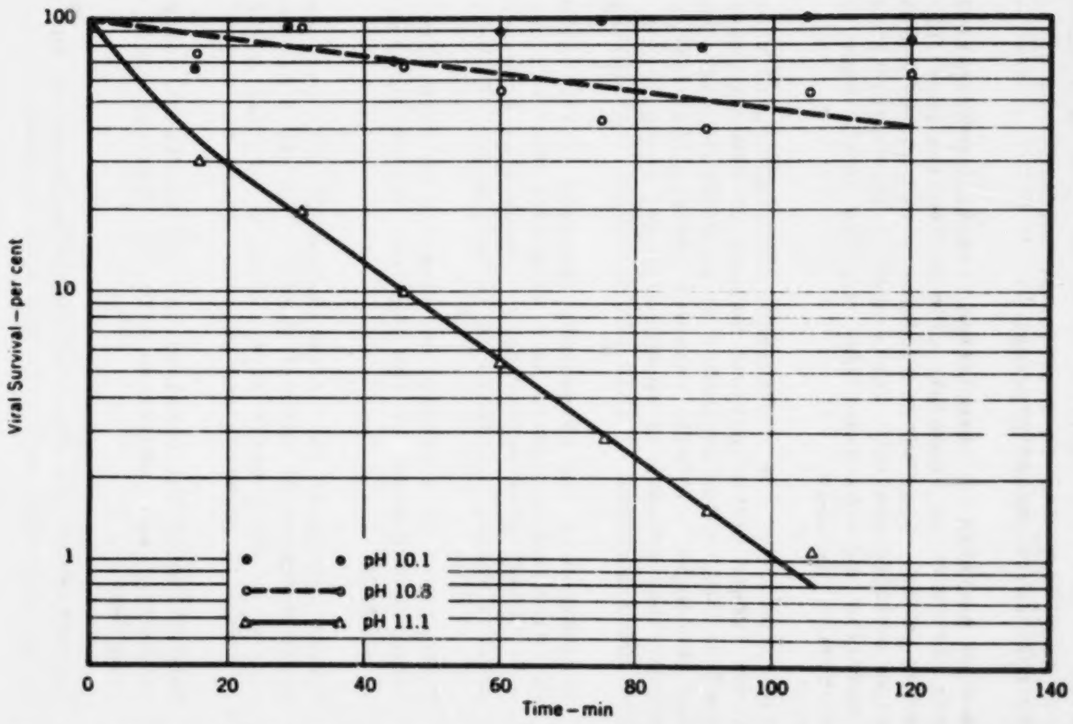


Fig. 1. **Effect of High pH on Poliovirus 1 (LSc) in Flocculated (500 mg/l $Ca(OH)_2$), Sand-Filtered Secondary Effluents at 25°C**

(from Berg et al.[28])

SECTION IV. THEORETICAL CONSIDERATIONS

Magnesium Equilibrium in Water

Magnesium is present to some extent in almost all natural waters. As a rule, magnesium content increases with increasing water hardness. The ratio of Mg^{++}/Ca^{++} is quite variable but almost always less than 1.

In Pearson's system of classifying metals,[29] magnesium is classed in group A, the same as aluminum. The elements of this group are visualized as having spherical symmetry with the electron sheaths not readily deformed by adjacent charged ions. Metals in this classification tend to form insoluble precipitates with OH^-, CO_3^{-2}, and PO_4^{-3} with simple electrostatic binding of cation and ligand used to explain complex stability.

In natural water systems, magnesium can be found in many solid phases. Considering only a system composed of carbln dioxide, magnesium, and water, one can calculate which solid phase controls magnesium solubility. The solid phases of magnesium present are:[45]

	ΔG^{o30} (KCal mol^{-1})	$-\log K_{so}^{30}$
1) Brucite - $Mg(OH)_2$		
$Mg(OH)_2(s) \rightleftarrows Mg^{++} + 2OH^-$	-15.8	11.6
$\log \frac{[Mg^{++}]}{[Mg(OH)_2{}^s]} = -pK_{so} + 2pK_w - 2pH$		
$\log [Mg^{++}] = 16.4 - 2pH$		
2) Magnesite - $MgCO_3$		
$MgCO_3(s) \rightleftarrows Mg^{++} + CO_3^=$	6.7	4.9
$\log [Mg^{++}] = -pK_{so} - \log_{C_T} - \log \alpha_2$		
$\log [Mg^{++}] = -4.9 - \log_{C_T} - \log \alpha_2$		

	Δ_G^{o30} (KCal mol^{-1})	$-\log K_{so}^{30}$
3) Nesquehonite - $MgCO_3 \cdot 3H_2O$		
$MgCO_3 \cdot 3H_2O(s) \rightleftarrows Mg^{++} + CO_3 + 3H_2O$	+7.4	5.4
$\log [Mg^{++}] = -pK_{so} - \log_{C_T} - \log \alpha_2$		
$\log [Mg^{++}] = -5.4 - \log_{C_T} - \log \alpha_2$		
4) Hydromagnesite - $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$		
$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O \rightleftarrows 4Mg^{+2} + 3CO_3^{-2}$		
$+ 2OH^- + 3H_2O$	+40.2	29.5
$\log [Mg^{++}] = -1/4pK_{so} + 1/2pK_2$		
$- 3/4 \log_{C_T} - 3/4 \log \alpha_2 - 1/2pH$		
$= -.4 - 3/4 \log_{C_T} - 3/4 \log \alpha_2 - 1/2pH$		

As Nesquehonite is less soluble than magnesite at all pH values, magnesite will not be considered. In Figure 2, a pH-stability diagram is shown for a total carbonate concentration of 10^{-3}M. Brucite is by far the least soluble at pH values above 9 with hydromagnesite controlling solubility from pH 9 to approximately 7.5. Nesquehonite is the least soluble at pH values below 7.5. Dolomite, $CaMg(CO_3)_2$, is a very common stable phase found in nature but attempts to precipitate a dolomite phase from supersaturated solutions under atmospheric conditions have been unsuccessful.[31]

Considerable effort has been expended in determining the solubility product-constant for $Mg(OH)_2$. The following table lists some of the values reported in the literature.

Investigator	t°C	pk_{SP}
Gallaher[32]	25-30	11.28
Ryzner *et al*.[33]	80	11.28
Krige and Arnold[34]	20	10.85
Travers and Nouvel[35]	18	10.60
Kline[36]	25	11.00
Britton[37]	Room	10.64
Bube[38]	25	10.92
Gjaldbach[39]	18	10.92
Dupre and Bialas[40]	18	10.92

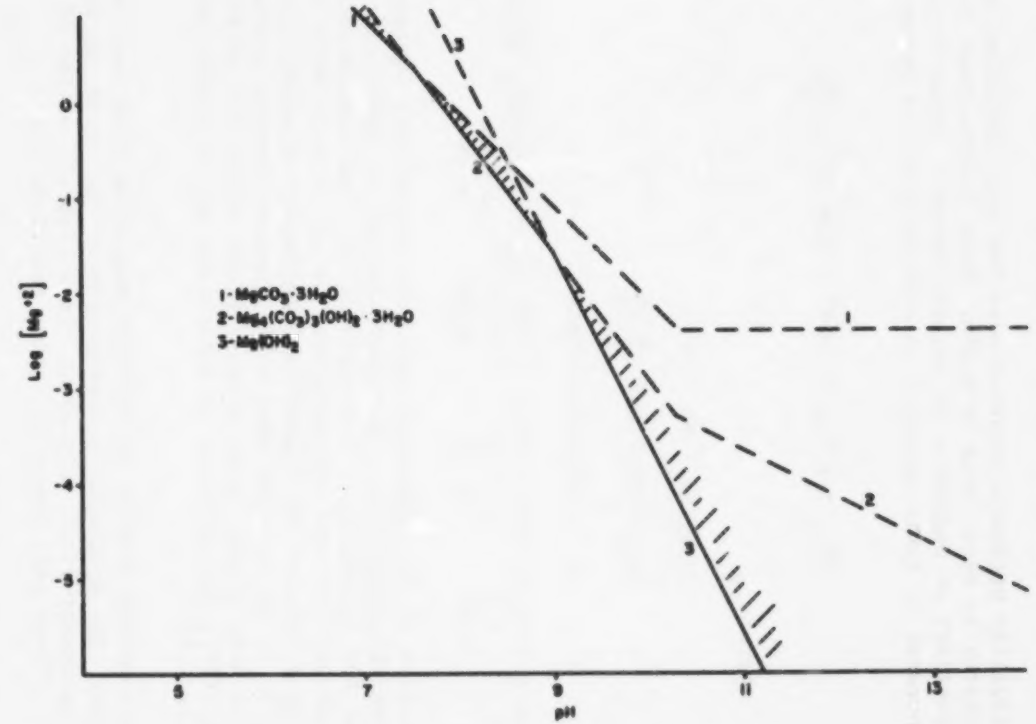


FIG. 2 SOLUBILITY DIAGRAM FOR MAGNESIUM IN WATER AT ATMOSPHERIC CONDITIONS. TOTAL CARBONATE = 10^{-3} M

(Stumm, W. and James J. Morgan. Aquatic Chemistry, Fig. 5-10)

Investigator	t°C	pk_{SP}
Herz and Muhs[41]	29	10.31
Kohlrausch and Rose[42]	18	10.87
Loven[43]	10	10.76

Magnesium hydroxide becomes less soluble at increased temperature. Figure 3 taken from Larson, Lane, and Neff[44] shows this effect.

The solubility products reported were for pure distilled water systems, extrapolated to zero ionic strength. Many factors tend to increase the solubility of magnesium in natural waters. Solubility increases with increase in ionic strength as expressed by the Debye-Huckel relationship:

$$pK_{so} = p^cK_{so} - (nZM^2 + mZN^2)\left(\frac{.5\sqrt{u}}{1+\sqrt{u}}\right)$$

where:

$$M_nN_m(s) \rightleftarrows nM + mN$$

$$K_{so} = [M]^n[N]^m A_M^n A_N^m$$

u = ionic strength

An illustration of this effect on the K_{sp} for $Mg(OH)_2$ using a $p^cK_{so} = 11.0$

	u = 0	u = .01	u = .1	u = .3
pK_{sp}	11.00	10.73	10.20	9.95

Complexation of the magnesium with both organic and inorganic ligands increases the solubility. The formation of ion pairs also tends to increase the solubility. Ion pairs differ from complexes in that the metal ion and the base are separated by one or more water molecules while for a complex the ligand is immediately adjacent to the metal cation.[45] It is reported that while complex formers present in solution may often have little or no effect on the solubility of solids, they may however affect the kinetics of nucleation and of growth and dissolution of crystals.[45]

Lime is commonly used to precipitate magnesium from water as magnesium hydroxide. The hydroxide concentration of the water can be increased to the necessary level only after converting all of the CO_2 and HCO_3^- to $CO_3^=$. These well known softening reactions are:

1) $CO_2 + Ca(OH)_2 \rightleftarrows \underline{CaCO_3} + H_2O$

2) $Ca(HCO_3)_2 + Ca(OH)_2 \rightleftarrows 2\underline{CaCO_3} + 2H_2O$

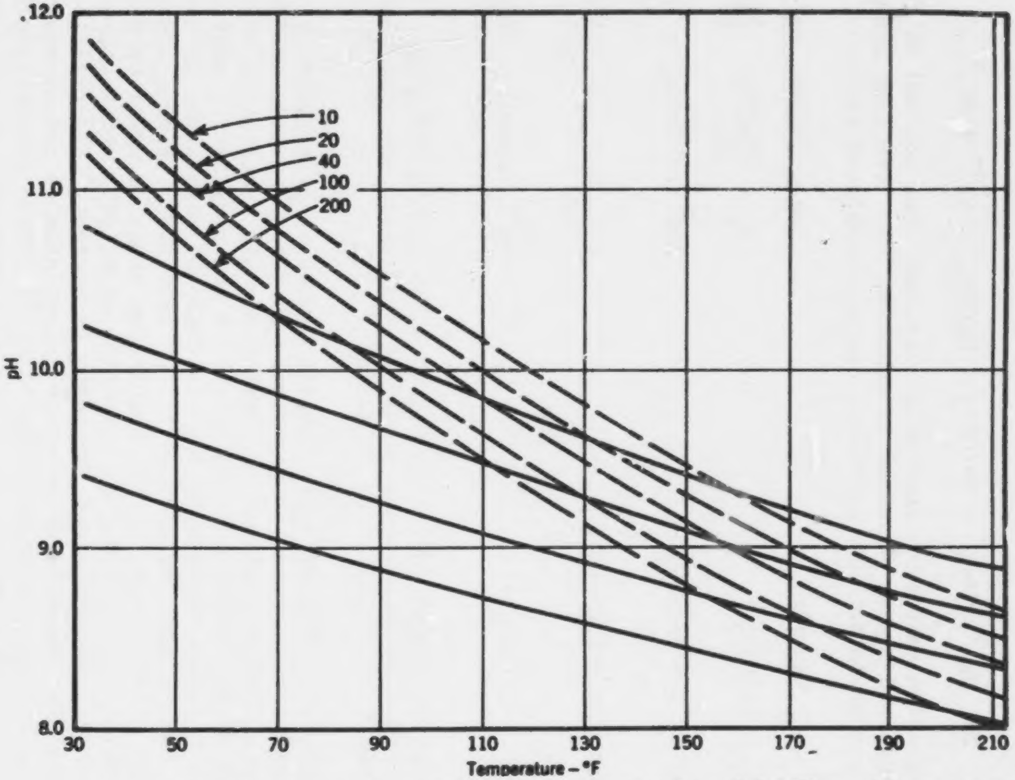


Fig. 3 **Temperature Influence on Magnesium Solubility** (from Larson, Lane, and Neff[44])

The dashed curves represent magnesium solubility (as parts per million $CaCO_3$); the solid curves, pH variation. The solubility curves are based on the solubility product constants of Travers and Nouvel.[35]

Magnesium bicarbonate is converted to magnesium carbonate and magnesium hydroxide on further addition of lime as:

3) $Mg(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons MgCO_3 + \underline{CaCO_3} + 2H_2O$

4) $MgCO_3 + Ca(OH)_2 \rightleftharpoons \underline{Mg(OH)_2} + \underline{CaCO_3}$

If the magnesium in the water is non-carbonate hardness, there would be no net change in total hardness, only an exchange of calcium for magnesium as:

5) $Mg^{++} + SO_4^{=} + Ca(OH)_2 \rightleftharpoons \underline{Mg(OH)_2} + Ca^{++} + SO_4^{=}$

Magnesium carbonate used as a coagulant does not add to the total dissolved solids as shown in equation (4). The lime dosages necessary for coagulation and softening can be calculated as:

Reaction	Lime required, mg/l of $Ca(OH)_2$
$CO_2 + Ca(OH)_2$	$CO_2 \times \frac{Ca(OH)_2}{CO_2} \; \frac{74}{44} =$
$2(HCO_3^-) + Ca(OH)_2$	Alk (as $CaCO_3$) $\times \frac{Ca(OH)_2}{CaCO_3} \; \frac{74}{100} =$
$MgCO_3 \cdot 3H_2O + Ca(OH)_2$	$MgCO_3 \cdot 3H_2O \times \frac{Ca(OH)_2}{MgCO_3 \cdot 3H_2O} \; \frac{74}{100} =$
$Mg^{++} + Ca(OH)_2$	Mg^{++} ($CaCO_3$) $\times \frac{Ca(OH)_2}{CaCO_3} \; \frac{74}{100} =$

In practice 90% pure lime CaO would be slaked and used. Thus, the total lime dosage found above should be multiplied by $\frac{100}{90} \frac{56}{74} \frac{CaO}{Ca(OH)_2}$ or 0.82 times the $Ca(OH)_2$ value determined.

$CaCO_3$ suspended in water has been found to be negatively charged while magnesium hydroxide is positively charged.[46] While the particles have been found to coexist, absorption usually takes place and one predominates, giving the floc either a net positive or negative charge. For a water containing both calcium and magnesium, the mobility tends to become less negative as the pH increases. Figure 4 demonstrates this effect found in the coagulation study of water used by Montgomery, Alabama. This is due to formation of $Mg(OH)_2$ which can cause charge reversal if sufficient magnesium is present. Flocculation of calcium carbonate suspensions using coagulant aids is not necessarily accompanied by a decrease in negative mobility.[46] These investigators reported that mobility in itself is not a reliable indicator of the degree of flocculation.

Salts other than magnesium carbonate could be used as the source of magnesium. Once the magnesium is recycled, it would be in the carbonate

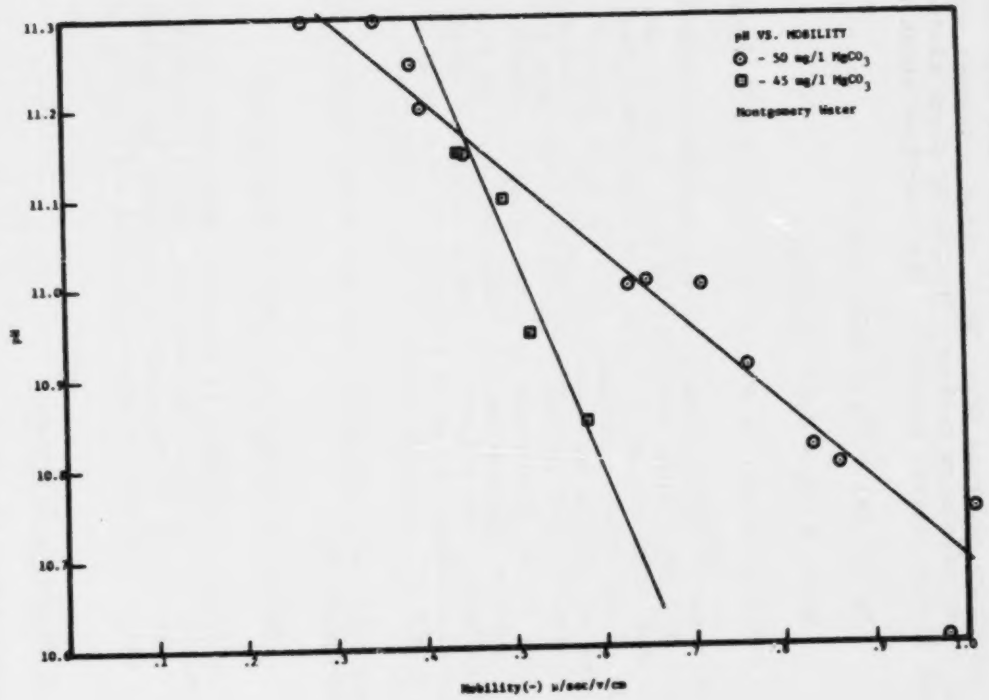


FIG. 4 EFFECT OF pH ON MOBILITY FOR THE INDICATED COAGULANT DOSAGES

or bicarbonate form. However any make-up magnesium salt, such as $MgSO_4$ or $MgCl_2$, would increase the non-carbonate hardness as shown in reaction 5.

Magnesium Recovery

As discussed in the introduction, the solubilization of magnesium by carbonation has been practiced by industry for many years. However, such processes have generally been carried out with supersaturated magnesium solutions and pure CO_2. While these processes must be carefully controlled, magnesium recovery from water plant sludges is quite simple, with little control required. The reactions which take place are:

$$Mg(OH)_2(s) + CO_2 \rightleftarrows MgCO_3 + H_2O$$

$$MgCO_3 + CO_2 + H_2O \rightleftarrows Mg(HCO_3)_2$$

Whether the reaction occurs in one or two steps is not known.

Black and Eidsness,[20] carbonating a sludge containing $Mg(OH)_2$ and 36 g/l of $CaCO_3$ with 11% CO_2, found that only 80 mg/l of $CaCO_3$ was dissolved after 30 minutes' carbonation at a gas flow five times that required to dissolve all of the $Mg(OH)_2$ present. According to Johnston,[47] who studied the solubility of calcium and magnesium carbonates in natural waters, the equilibrium ratio at 16°C is $[Mg^{++}]/[Ca^{++}] = 14{,}000$ when the partial pressure of CO_2 in the atmosphere is great enough to prevent precipitation of $Mg(OH)_2$. Another explanation for these phenomena is that a saturated solution of $Ca(HCO_3)_2$ has a lower pH than a saturated solution of $Mg(HCO_3)_2$. As carbonation proceeds, the pH is buffered at a pH of approximately 7.5, due to the $Mg(HCO_3)_2$, allowing little of the calcium to dissolve.

Magnesium hydroxide may also react with the bicarbonate to produce magnesium carbonate as:

$$Mg(OH)_2 + Mg(HCO_3)_2 + 2H_2O \rightleftarrows 2MgCO_3 \cdot 3H_2O$$

If complete solution of $Mg(OH)_2$ is desired, obviously precipitation of $MgCO_3 \cdot 3H_2O$ should be avoided. In practice, this is avoided by incremental addition of fresh sludge to the carbonation basin and maintaining a sludge-water ratio such that a super-saturated solution of $Mg(HCO_3)_2$ is not produced.

Production of Magnesium Carbonate

At present magnesium carbonate is produced from four major sources.[48]

1) From sea water without evaporation, using sea water and lime as the principal raw materials.

2) From bitterns or mother liquors from the solar evaporation of sea water for salt.

3) From deep-well brines.

4) From dolomite.

Investigators are not in agreement regarding the formulae for the several forms of magnesium carbonate. For this dissertation it will be assumed that at least three salts may be prepared by aerating an aqueous solution of magnesium bicarbonate: the penta-hydrate $MgCO_3 \cdot 5H_2O$ precipitated below 13.5°C; the tri hydrate $MgCO_3 \cdot 3H_2O$ precipitated between 13.5°C and 50°C and a "basic carbonate" whose composition is most commonly given as $4MgCO_3 \cdot Mg(OH)_2 \cdot x\ H_2O$ precipitated above 50°C, most rapidly and completely by boiling. Both the penta-hydrate and the tri-hydrate slowly revert to the basic carbonate, $5MgO \cdot 4CO_2 \cdot xH_2O$, upon exposure to the atmosphere. This reversion is accelerated when moisture is present and at elevated temperatures. When heated to 100°C, dry $MgCO_3 \cdot 3H_2O$ is quite stable.[49] $MgCO_3 \cdot 3H_2O$ exhibits an interesting change in solubility on heating to 100°C. Figure 5 demonstrates this increased solubility effect. The data for this figure were collected from analytical studies of the $MgCO_3 \cdot 3H_2O$ sludge produced in Dayton, Ohio. It is assumed that the conversion to the basic carbonate involves recrystallization of the aqueous solution. At 200°C, dry material loses water and CO_2 without the addition of water. Possibly partial decomposition furnishes some water which can then assist further conversion.[49]

Magnesium carbonate, which is used primarily in the paint, printing, rubber and pharmaceutical industries, sells from $.16/lb for the technical grade to $.22/lb for the USP grade.[50] Most of the product produced today is the basic carbonate, $4MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$.

As discussed in the introduction, a new source of magnesium carbonate will be soon available at a greatly reduced cost. A process has been developed by A. P. Black and the city of Dayton, Ohio to recover it from water softening plant sludges.[23] Preliminary calculations, included in the appendix, indicate that as much as 150,000 tons of magnesium carbonate ($MgCO_3 \cdot 3H_2O$) can be produced each year by the twenty cities shown. Substitution of recycled $MgCO_3 \cdot 3H_2O$ for alum in the more than 4,000 water treatment plants now using it would require approximately 100,000 tons per year, assuming 85% recovery and re-cycling of the magnesium and 15% make-up. These calculations are also included in the appendix.

The cost to produce $MgCO_3 \cdot 3H_2O$ with this new technology has been estimated to be less than $.02/lb.[51]

Colloidal Destabilization

Colloidal destabilization is believed to occur in two steps. The first, which is assumed to occur very rapidly, has been referred to as perikinetic coagulation[52] or coagulation.[53] In this step, chemical and physical interaction between the colloid to be removed and the coagulant takes place. Two broad theories have been advanced to explain the mechanism. The older, chemical theory, assumes stabilization to be due

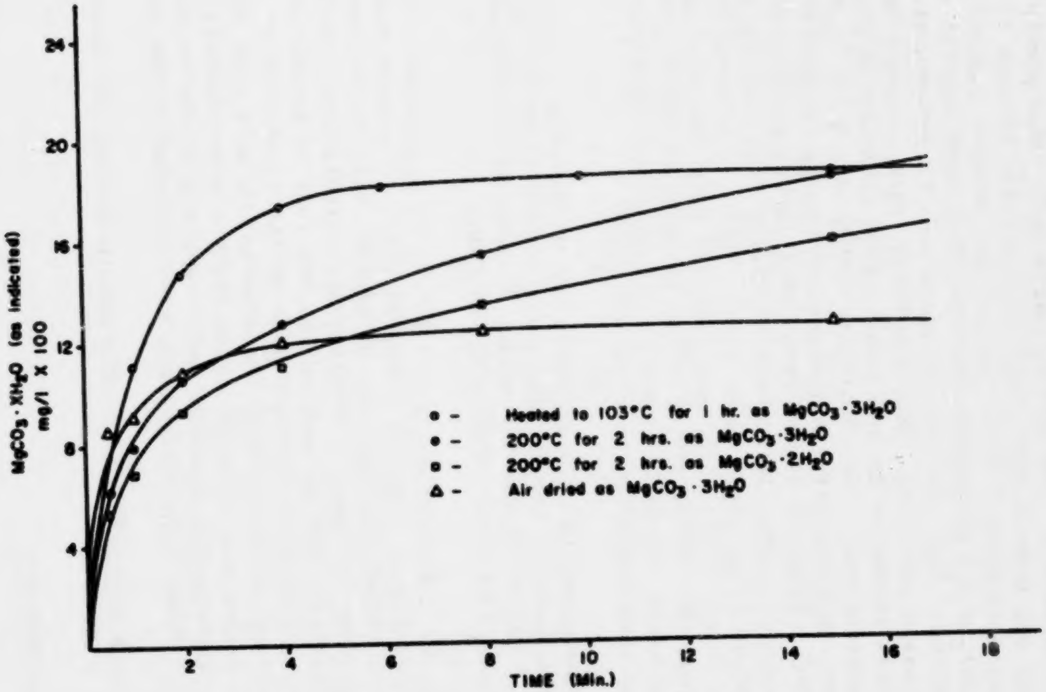


FIG. 5 SOLUBILITY OF $MgCO_3 \cdot XH_2O$ AS A FUNCTION OF TIME FOR THE INDICATED HYDRATE FORMS

to chemical interactions, such as complex formation and proton transfer. The physical theory emphasizes the concept of the electrical double layer. Counter-ion adsorption and compaction of the diffuse portion of the double layer are assumed to neutralize the colloidal charge and bring about coagulation.

After coagulation, orthokinetic coagulation[52] or flocculation[50] takes place, normally requiring a longer time period with gentle mixing conditions. During this step, interparticle bridging of the coagulated colloids forms larger floc particles.

The first coagulants, alum and iron salts, were chosen for their highly gelatinous properties. Later investigators attributed the Shultz-Hardy[54,55] effect as the main attribute of these coagulants.[56] However, more recent investigators found that the hydrolysis products were much more effective than the trivalent metal cations.[52,57,58] Many investigators have reported the effect of anions on the broadening of the optimum pH for coagulation.[56,57,59] The displacement of hydroxide ions by highly coordinating anions has been proposed as the mechanism for these phenomena.[60]

In 1928, Mattson[61] demonstrated the relationship between microelectrophoretic mobility of colloidal particles and the aluminum salt dosages. However, this technique remained almost forgotten until 1959 when Pilopovich _et al_.[58] studied the effects of pH, alum dosage, zeta potential, and base exchange capacity of clay particles on coagulation. Several investigators reported that base exchange capacity was an important factor in coagulation.[52,58] It was also found that, while good coagulation often occurred near zero mobility, no absolute relationship existed.[58]

In a series of papers, Packham proposed that coagulation was due almost entirely to a physical enmeshing or sweeping down of particles by the highly gelatinous property of the aluminum hydrolysis products.[57] He found that the type of dispersed phase had relatively little effect on coagulation conditions. Packham's work and other recent investigators seem to support the early contentions that the sticky, gelatinous, property of a coagulant is possibly most important. The mechanism of coagulation seems to be dependent upon the properties of the dispersed phase and the conditions which are present during coagulation.

Chemical and Physical Properties of Organic Color

While the origin of organic acids found in natural waters is still a subject of controversy, most investigators report that it is due to aqueous extraction from soil or decaying vegetation. Some investigators propose that color in water is an intermediate step in the transformation of organic matter from living or decaying woody tissue to the soil organic complex.[62]

The structure of the organic acids has been proposed to be aromatic with hydroxy, carboxy, methoxy, and carboxylic acid groups.[62] Black and Christman, using an electrodialysis cell with membranes of varying pore sizes, found that 78% of the organic acid molecules were between 3.5 and 10 mμ.[63] However, light scatter data for this same organic color suggested a larger size.[64] An elemental analysis of organic color extracted from ten highly colored natural waters gave the following range of results.[63]

Carbon - 44.99 - 54.10%
Hydrogen - 3.86 - 5.05%
Nitrogen - 1.46 - 4.23%
Oxygen - 38.76 - 47.93%

Some investigators have found nitrogen present, but the carbon/nitrogen ratio is reported to be higher for more highly colored lakes indicating nitrogen as an impurity.[64] The molecular weight of the colored acids is generally believed to range from 450 to 10,000. However Gjessing, using Dioflo ultra-filtration membranes reported approximately 85 percent of the organic acids present had a molecular weight higher than 20,000.[65]

Kitano observed that organic acids influenced inorganic solubility equilibrium and subsequent precipitation products.[66] Shapiro has found considerably more iron in solution in natural waters than would be predicted by theoretical solubility equilibria.[67] He proposed peptization of the iron by humic acids with some chelation as the possible mechanism. Oldham and Gloyna[68] propose the mechanism for increased iron solubility to be the ability of the humic acids to reduce Fe^{+3} to its more soluble form Fe^{+2} and the subsequent complexation of the iron by the humic acids.

Color has been found to vary in intensity as a function of pH. Singley et al.[69] have developed a nomograph which will correct the color intensity at any pH to that at pH 8.3, an arbitrary standard.

Black et al.[70] have found a stoichiometric relationship between the ferric sulfate dosage required for satisfactory color removal and the raw water color in a study of colored waters from different regions of the United States.

SECTION V. EXPERIMENTAL MATERIALS AND METHODS

Research efforts should of necessity begin with controlled basic systems and advance in complexity as information is obtained. This study begins with synthetic water, where system variables can be established so it is possible to study a single variable at a time. Many methods have been employed to evaluate coagulation processes[78] but the jar test has been the most widely used and was the primary method chosen for this study. An improved version of the jar test apparatus was used. The jar test consists of a series of jars, containing the adjusted parameters under study, with mixing provided to simulate actual plant conditions. Normally a settling period follows mixing, where settling can be evaluated. Modifications have been made in order to increase the information obtained. The parameters measured during this study included:

1) Coagulation pH
2) Forms of alkalinity and hardness
3) Settled color and turbidity
4) Electrophoretic mobility
5) Residual magnesium
6) Hardness, alkalinity and color of stabilized water
7) Visual observation of floc properties and settling rates.

Coagulant recovery was studied in detail for both synthetic and natural waters. A volume of water was coagulated to produce from one to two liters of sludge which was then carbonated, monitoring calcium, magnesium and organic color released. The recovered magnesium was reused in order to evaluate any change in coagulation effectiveness. Some filtrability studies of the carbonated sludge were performed.

Montmorillonite and Emathlite Clay Suspensions

The montmorillonite was montmorillonite #23 (Bentonite) obtained from Ward's Natural Science Establishment, Inc., Rochester, New York. The emathlite was obtained from Mid-Florida Mining Company, Lowell, Florida.

Organic Color

Approximately 160 liters of highly colored water was collected from runoff in the Austin Carey Forest, near Gainesville, Florida. The water was very low in turbidity and ionic strength.

Magnesium Carbonate

The magnesium carbonate was prepared from water softening plant sludge at Dayton, Ohio. The wet magnesium carbonate was shipped to Gainesville where it was air dried. The analysis for alkalinity and magnesium of a solution containing .5g of the material allowed calculation of the hypothetical formula, which was found to be the tri-hydrate of magnesium carbonate, $MgCO_3 \cdot 3H_2O$. A chemical analysis performed by the Research and Analytical Laboratory of the Monsanto Chemical Company, Dayton, Ohio, of a similar batch of magnesium carbonate produced in April of 1970 indicated the following composition:

Constituent	Percent by Weight
Magnesium Oxide, MgO	29.44
Calcium Oxide, CaO	0.07
Carbon Dioxide, CO_2	32.50
Silicon Dioxide, SiO_2	<0.01
Aluminum Oxide, Al_2O_3	0.005
Ferric Oxide, Fe_2O_3	<0.01
Sulfur Trioxide, SO_3	<0.01
Chloride, Cl^-	<0.001
Total Insolubles	<0.01
Loss on Ignition	70.67

Flocculant Aids

The flocculant aids studied included an anionic potato starch, Hamaco 196, Alum, AP[30], and activated silica.

Synthetic Water Constituents

Reagent grade $CaCl_2$, $NaHCO_3$, and K_2SO_4 were used to prepare stock solutions for adjusting the calcium, alkalinity, and sulfate concentrations of the synthetic water.

Preparation of Clay Suspensions

Both clays were pulverized by jar milling for twenty-four hours. Approximately 20 grams of the pulverized clay and 10 grams of reagent grade sodium chloride were added to four liters of water. The slurry was mixed for twenty-four hours and then dewatered using No. 40 Whatman filter paper in a Buchner funnel. The clay was washed with distilled water and resuspended in four liters of distilled water. After several hours of mixing, the slurry was allowed to settle to remove the larger clay particles. The supernatant was withdrawn for use as a stock turbidity solution.

This process was similar to that used by Black and Hannah[79] to give a more uniform suspension, allow greater precision of measurement, and to promote exchange reactions due to the high zeta potential associated with the sodium form of the clay. These authors, using the same clays, found the base exchange capacity of fullers earth to be 26.5 milliequivalents per liter and that of the montmorillonite to be 115 milliequivalents per liter. The base exchange capacities of these clays were determined by the ammonium acetate method used in soil analysis.[80]

Preparation of Organic Color Concentrate

A highly concentrated, pure form of naturally occurring organic color was needed. Various methods have been employed to concentrate organic color such as vacuum distillation, carbon adsorption, freezing and ion exchange. Vacuum distillation was chosen because of its simplicity, availability of a large vacuum still, and reportedly minor effects on the chemical nature of organic color.

The water collected was first filtered through Whatman 41 ashless filter paper. The color was then concentrated using a Precision Scientific Flash evaporator. The operating vacuum was maintained by a vacuum pump at 4-6 cm of mercury and a temperature of less than 40°C. The capacity of the vacuum pump limited the evaporation rate to about 2.5l/hr.

The evaporation procedure was semi-continuous. The feed rate was adjusted to match the evaporation rate. When the color in the evaporator reached the desired concentration, the evaporator was emptied and the procedure repeated.

The color concentrate was filtered through a series of Whatman 40 + 41 paper then through Millipore .8μ and .45μ filters. The concentrated color was then placed in dialysis tubing and dialized against distilled water for twenty-four hours. Chemical analyses of the untreated, concentrated, and treated concentrate are shown in Table 1. All chemical analyses were run in accordance with the procedures outlined in Standard Methods with metal ion determined by atomic absorption analysis. The two batches of raw water were collected to obtain the desired volume of color concentrate. The color concentrate was stored at 4°C in tightly stoppered liter bottles.

Preparation of Synthetic Waters

A synthetic water whose composition was designed to represent, as nearly as possible, a typical soft surface water of low alkalinity and total hardness was prepared from the stock solutions listed elsewhere.

The synthetic stock solutions were prepared using deionized distilled water so that 1 ml = 50 mg of Ca(as $CaCO_3$), alkalinity (as $CaCO_3$) and $SO_4^=$. Working solutions were prepared by diluting these stock solutions 10 to 1 with deionized distilled water so that 1 ml = 5 mg of the desired constituents.

The synthetic water had the following composition:

TABLE 1

CHEMICAL ANALYSIS OF ORGANIC COLOR

	Raw #1	Raw #2	Concentrate	Filtered and Dialized Concentrate
pH	4.70	4.45	4.00	4.40
Conductivity (μmho/cm)	48.5	57.5	520	230
Color (pH 8.3)	700	690	15,150	13,250
Acidity (mg/l $CaCO_3$)	20.1	25.0	320	200
COD (mg/l)	117	108	2,660	2,010
TS (mg/l)	0.190	0.182	2.76	2.00
VSS (mg/l)	0.103	0.983	2.08	1.66
NH_3N (mg/l)	0.41			
Organic N (mg/l)	3.14			
TOC (mg/l)	39.5			
C/N Ratio	12.6			
ZN (mg/l)	< .1	<.1	1.20	1.20
Cu (mg/l)	0.04	0.04	0.40	0.20
MN (mg/l)	0.03	0.04	0.70	0.45
Fe (mg/l)	8.2	6/4	106	98
Mg (mg/l)	1.3	1.0	18	1 0
Na (mg/l)	5.1	4.3	8.2	2.3
Ca (mg/l)	1.9	1.2	8.0	5.0

	Concentration Factor
Color	21.8
COD	22.8
Acidity	15.9
Conductivity	10.3
Volume	26.7

Milliequivalents	ppm	Milliequivalents	ppm
Ca^{++} ------0.500	10.0	HCO_3^- ------0.500	30.5
Na^{++} ------0.500	11.5	SO_4^{-2} ------0.500	24.0
K^+ ------0.500	19.5	Cl^- ------0.500	17.7
1.500		1.500	

Total alkalinity as $CaCO_3$ ------------- 25 ppm
Total hardness as $CaCO_3$ ------------- 25 ppm
Total dissolved solids -------------114 ppm

Alum

The alum stock solution was prepared by adding reagent grade aluminum sulfate to deionized distilled water so that 1 ml was equal to 10 mg of aluminum sulfate. This solution was stored at 4°C and used daily to prepare working solutions by dilution with distilled water so that 1 ml = 1 mg of aluminum sulfate.

$MgCO_3 \cdot 3H_2O$

For dosages of less than 15 mg/l of $MgCO_3 \cdot 3H_2O$, it was added as a solution containing exactly 0.5000 g of the material in 1 liter of demineralized water. Fresh solutions were prepared weekly.

When dosages greater than 15 mg/l were to be used, they were accurately weighed into 15 ml beakers and quantitatively transferred to the stirred water sample as a slurry. In the case of synthetic waters, deionized water was used to prepare the slurry; for natural waters, the water itself was used.

Flocculants

Alum:

A fresh solution containing 0.1 mg/ml of $Al_2(SO_4)_3 \cdot 18H_2O$ was prepared daily from a stock solution stored at 4°C.

Starch:

The starch solution was prepared daily by slowly sifting 1.0 gram of starch into 1 liter of deionized distilled water and rapidly mixed with a magnetic stirrer. A working solution was prepared by diluting 10 to 1 with deionized distilled water so that 1 ml = 0.1 mg of starch.

Activated Silica:

The activated silica solution was prepared and activated in the following manner:

1) 10 ml of distilled water was added to a 100 ml graduated cylinder.

2) 5 ml of 348 gram/l solution of "N" brand sodium silicate added.

3) 5 ml of 1 N NH_4Cl was added with constant stirring to the graduated cylinder.

4) After 5 minutes' aging, the solution was made up to 100 ml volume with distilled water and mixed thoroughly.

Determination of Turbidity and Color

A Lumetron Model 450 Filter Photometer was used for both color and turbidity determinations. Sufficient accuracy was obtained using the red 650 mμ filter and 75 mm cell light path for turbidity determinations. A calibration curve was prepared plotting optical density obtained for a sample against the turbidity values previously obtained for the sample using a Jackson Candle Turbidimeter as described in Standard Methods.[81] The turbidity solutions used for this calibration procedure were prepared using the emathalite clay stock solution.

Organic color was measured using a 560 mμ filter and the 75 mm cell light path. The calibration curve for color was obtained by plotting optical density as a function of various dilutions of Platinum-Cobalt Color Standard.

When color and turbidity were both present in a sample, a procedure outlined in the Lumetron Operating Manual[82] was followed. This procedure takes advantage of the fact that organic color absorbs light more strongly at shorter wave lengths. Color would therefore have little interference in the measurement of turbidity. The following procedure was used to determine color in the presence of turbidity:

1) For various levels of turbidity the optical densities were measured at 650 mμ. An average value was determined for the ratios between the optical density at 560 mμ and 650 mμ. This average value represents a constant for any level of turbidity and will be denoted as $\underline{R}$.

2) The optical density of the sample was determined at 560 mμ and 650 mμ.

3) $\underline{R}$ multiplied by the optical density at 650 mμ represents the interference due to turbidity. Subtracting this product from the optical density found at 560 mμ gives a value which can be used to determine the color from the calibration curve previously prepared.

Atomic Absorption

Iron, sodium, magnesium, and calcium were determined by use of a Model 1301 Beckman Atomic Absorption Unit in combination with a Beckman DBG Grating Spectrophotometer and Beckman Potentiometric Recorder with scale expander. The procedures outlined in Methods for Analyses of Selected Metals in Water by Atomic Absorption[83] were followed. The standards were prepared as described with the exception of iron, for which reagent grade ferrous ammonium sulfate was used to prepare the standard solution. A calibration curve was obtained each time the samples were run, plotting absorbance versus concentration.

Electrophoretic Mobility

The electrophoretic mobility determinations were made using a Zeta-Meter. The samples were analyzed immediately after collection using the 8 power microscope objective and a two-hundred volt potential. The procedure outlined in the Zeta-Meter Manual[84] was followed for all determinations. Normally 10 particles were tracked for each sample.

Stabilization of Treated Waters

In order to make possible a comparison of both physical and chemical parameters of waters coagulated with magnesium and with alum, all samples were stabilized to pH 9.0. Waters coagulated with $MgCO_3$ were stabilized with CO_2. Those coagulated with alum were stabilized with freshly filtered, saturated lime water.

Stabilization of Water Coagulated with Alum:

Approximately 300 ml of settled water, filtered if necessary, was transferred to a 500 ml beaker, placed on a magnetic stirrer and titrated with clear saturated lime water to pH 9.0, measured by a glass electrode. The sample was then filtered through Whatman No. 40 paper and color, total alkalinity, total hardness, calcium and magnesium determined.

Stabilization of Water Coagulated with Magnesium Carbonate:

Approximately 300 ml of settled water was transferred to a 500 ml beaker, placed on a magnetic stirrer, approximately 1 g of reagent grade powdered $CaCO_3$ added and the suspension carbonated by blowing through a pipette with rapid mixing. Three to five minutes were required to reduce the pH to 9.0, measured by a glass electrode, as above. The suspension was then filtered through Whatman No. 40 paper and color, total alkalinity, total hardness, calcium and magnesium determined.

Alkalinity

The alkalinity titrations were performed using 0.02 N H_2SO_4 with phenolphthalein and methyl purple indicators as described in Standard Methods. The sulfuric acid was standardized using standard 0.02 N sodium carbonate, also as described in Standard Methods.

Hardness

Total and calcium hardness were determined by titrating with carefully standardized EDTA, following exactly the procedures as described in Standard Methods. Many determinations were checked by atomic absorption.

pH Measurement

All pH measurements were made using a Corning Model 7 pH Meter with a Corning Combination glass and Ag/AgCl, electrode. The pH meter was calibrated daily using solutions prepared from concentrated standard buffer solutions purchased from W. H. Curtin and Company.

Jar Test Procedures

The jar test procedures were very similar for the natural and synthetic waters and the discussion will be applicable to both series. The procedure outlined will follow chronological order with the differences between the series discussed in the order in which they occur. In every instance where magnesium is used, it is added in the tri-hydrate form, $MgCO_3 \cdot 3H_2O$. In this text and tables it has been referred to as magnesium carbonate or $MgCO_3$.

Preliminary Determinations:

Chemical and physical analyses were performed on each natural water prior to jar testing. These tests included pH, color, turbidity, alkalinity, hardness, and magnesium. A sample of each natural water was filtered through No. 40 Whatman filter, acidified to approximately pH 2 with concentrated HCl, and stored in a glass bottle for analysis by atomic absorption for magnesium and iron.

The coagulant dosages were chosen to give undertreatment of the water at the lower dosages and overtreatment at the higher dosages. Based on previous experience, this range in chemical dosages could usually be determined from the results of the chemical and physical analyses. For synthetic waters, these parameters were, of course, chosen for each jar test.

For both, the quantity of water to total 1 liter after the addition of all dosages was calculated and added to each jar.

Details of Jar Test Procedure:

For studies where the magnesium carbonate was added as a slurry, at least two minutes of mixing at 100 RPM was provided after the slurry addition. The lime slurries were then added to the jars. The initial addition required approximately one minute with two additional minutes needed to rinse the six beakers in order to complete the quantitative transfer of the lime slurry. When flocculant aids were used, they were added approximately three minutes after the lime addition. Incremental addition of starch was evaluated using six dosages, one minute apart. Three were added during rapid mix and three during the flocculation period.

Samples for electrophoretic mobility determinations were taken during rapid mixing, approximately one minute after flocculant aid addition or approximately three minutes after lime addition when no flocculant aid was used. The mixing speed was then slowed to 10 to 12 RPM and maintained for 15 minutes. After visual observations of the floc characteristics, 100 ml samples were collected and filtered through Whatman No. 40 paper for immediate determinations of alkalinity.

After the flocculation periods, mixing was stopped and the jars allowed to settle for twenty minutes. At that time samples of the supernatant were taken for color and turbidity analysis. pH determinations were then made on all jars and the water in selected jars was stabilized, filtered and analyzed.

The studies using alum were performed in a similar manner. For several very low alkalinity waters pre-lime was added first, using a saturated calcium hydroxide solution to increase the total alkalinity of the water. Electrophoretic mobilities were not determined on these waters.

Recovery Studies

The recovery of magnesium from the sludges produced in coagulating both synthetic and natural waters was evaluated. The synthetic waters were prepared to give a range in organic color of from 15 to 200 and a montmorillonite turbidity range of from 15 to 50. Coagulation was carried out in a forty-liter Pyrex jar using a small Lightning mixer with a rheostat to control the mixing. The quantity of water to total 36 liters after the addition of all dosages was added to the jar. The salt solutions were then added using the concentrated stock solutions to reduce the volumes added.

As before, coagulant dosages were estimated from previous jar tests. The magnesium carbonate was vigorously slurried and quantitatively added to the rapidly mixed water. After approximately three minutes, the lime slurry was added. Five minutes after the lime addition, the alum was added and the rapid mixing continued for two additional minutes. The mixing was then slowed and maintained for twenty minutes at a speed which would deep the floc in suspension.

The floc was allowed to settle for a period between several hours and overnight in some cases. The clear supernatant was carefully syphoned from the sludge layer and a composite sample collected for analyses.

The sludge was then poured into a 2 liter graduated cylinder and measured. In all but the first two experiments the volume was then made up to 2 liters with distilled water before carbonation.

Sludge Carbonation

Carbonation of the sludge was performed using a cylinder of specially prepared gas containing 15% CO_2 and 85% air. A 2 liter graduated cylinder was placed on a large magnetic stirrer for continuous mixing during carbonation. The flow of CO_2 was regulated using a gas pressure regulator, so that fine, well dispersed bubbles were produced. A carborundum stone diffuser was used to disperse the CO_2 into the sludge with no attempt made to measure the gas flow rate.

Fifty-milliliter samples were taken at predetermined time intervals and filtered through Whatman No. 40 filter paper. pH determinations were made on the filtrate; 10 ml samples were titrated for alkalinity, and a dilution of the remainder prepared for color analysis. After organic color had been determined, the samples were acidified and stored for future analysis for magnesium and calcium by atomic absorption. The sludge was carbonated in most cases until a pH in the range of 7.5 to 7.0 was reached.

The remaining sludge was filtered through No. 40 Whatman paper using a vacuum flask and Buchner funnel. Several filterability studies were made using polymers and calcium carbonate as filter aids. Two general methods of evaluation were employed - determination of the time to dewater 100 ml of the sludge and determination of the total volume that could be filtered before clogging occurred.

Separan AP[30] was used in the polymer evaluation. Incremental addition of 1 mg/l of the polymer, followed by determination of the time for filtration of 100 ml of the sludge provided data used to determine the effect of the polymer on sludge filterability.

The filtrates from several of the recovery studies were stored to be used as recycled coagulant.

Coagulation Using Recovered Magnesium Bicarbonate

Coagulation, using both the standard jar test apparatus and the 40 liter Pyrex jar with the variable speed Lightning mixer, was evaluated using recovered magnesium. The required volume of recovered magnesium bicarbonate to give the desired coagulant dosage was added and the coagulation tests performed as discussed previously.

The coagulation of selected synthetic and natural waters was repeated, using the solutions of magnesium bicarbonate recovered as described above, and results identical with those obtained with the original magnesium carbonate were obtained. This was done with jar tests and with "recovered coagulant in the 40 liter vessel.

SECTION VI. RESULTS AND DISCUSSION

Coagulant Studies of Synthetic Waters

Emathlite clay turbidity was used in the first studies of synthetic waters, since clays of this type have been employed by others for coagulation studies. An experiment was designed to determine the relationship between the level of turbidity and/or organic color present and the dosage of magnesium carbonate required for satisfactory treatment of the water. The alkalinity and hardness were held constant at 25 mg/l as $CaCO_3$. An acceptable treatment would give a settled turbidity less than 3.5 mg/l and color less than 15 mg/l. A minimum of six jars were required to determine the lowest dosage of magnesium carbonate for each combination of color and turbidity. Table 2 summarizes the data used in the development of this relationship for emathlite turbidity.

TABLE 2

MAGNESIUM CARBONATE REQUIRED FOR COAGULATION OF ORGANIC COLOR AND EMATHLITE TURBIDITY

$MgCO_3$	Color	Turbidity
4	15	60
20	50	60
90	200	60
20	50	20
90	200	20
90	200	100
10	50	100
50	100	100

A stepwise, linear regression equation was calculated using a BMD02R Computer Library program.[85] The general form of the regression equation was:

$$Y = A + b_1X_1 + b_2X_2$$

where:

Y = magnesium carbonate dose
A = constant
X_1 = the variable, either color or turbidity, which is most significant in reducing the total sums of squares
X_2 = the variable remaining
b_1 = regression coefficient for X_1
b_2 = regression coefficient for X_2

The equation resulting is;

$$Y = -3.95 + .48 \text{ color} + .02 \text{ turbidity}$$

For the data shown, color and turbidity account for 98.67% of the variations in the required magnesium dosage with a highly significant F value of 440^{86} and standard error of the estimate of 5.22.

Lime along with a flocculant, starch, was found to satisfactorily flocculate the emathlite turbidity as shown in Table 3. Possibly the fine particles of turbidity served as a nucleii for calcium carbonate precipitation which was in turn agglomerated by the starch to a size which would settle.

Magnesium carbonate's effectiveness in color removal is demonstrated in Table 4. The color present seemed to improve the size of the floc as well as its settleability. No attempt was made to measure the magnesium in solution after coagulation in these early experiments. It was found however, that good floc formation took place at a pH above 11.0; therefore the pH of coagulation was maintained from 11.0 to 11.25.

The experiments with montmorillonite clay turbidity were designed in a similar manner to determine the effect of color and turbidity on the coagulant dosage. The data used to develop this relationship are shown in Table 5 below:

TABLE 5

DOSAGE OF $MgCO_3$ REQUIRED TO COAGULATE ORGANIC COLOR AND MONTMORILLONITE TURBIDITY

$MgCO_3$	Color	Turbidity
85	200	20
90	200	100
80	200	60
15	50	20
15	50	100
15	50	60
40	100	100

The equation determined is:

$$Y = -10.24 + .47 \text{ color} + .03 \text{ turbidity}$$

Color and turbidity account for 99.41% of the variation in required magnesium dosage with a highly significant F value of 710 and standard error of the estimate of 3.24. As with the emathlite turbidity, lime, aided by a flocculant, was satisfactory in removing montmorillonite clay turbidity. In Table 6, the effectiveness of $MgCO_3$ in color and

TABLE 3

COAGULATION OF FULLER'S EARTH TURBIDITY WITH $MgCO_3$ AND WITH LIME

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Ha 196					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	0	95	0.4	10.80		3.3		46	56	0										
2	2	97	0.4	10.90		2.1	-.95	50	48	0										
3	4	100	0.4	10.95		2.0	-.42	58	44	0										
4	6	102	0.4	10.95		1.6	-.54	52	44	0										
5	10	105	0.4	10.95		1.5	-.36	58	44	0										
6	15	110	0.4	10.95		1.0	-.40	62	40	0										

Characteristics of raw water

Alkalinity as $CaCO_3$ 25
Total Hardness as $CaCO_3$ 25
pH. 8.30
Organic Color 0
Turbidity 100
Type Clay . . . . . . Emathlite Clay

Comments

TABLE 4

COAGULATION OF A SYNTHETIC WATER CONTAINING BOTH ORGANIC COLOR AND FULLER'S EARTH TURBIDITY WITH $MgCO_3$

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Ha 196					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	75	130	0.4	11.10	>50	10.0		60	118	0										
2	100	144	0.4	11.10	>25	2.0		69	78	0										
3	120	155	0.4	11.05	14	1.5		59	52	0										
4	140	166	0.4	11.05	10	1.2		62	40	0	9.0	9	0	52	52	1	53			
5	160	177	0.4	11.10	12	1.9		50	44	0										
6	180	188	0.4	11.10	16	3.8		43	48	0										

Characteristics of raw water

Alkalinity as $CaCO_3$ 25
Total Hardness as $CaCO_3$ 25
pH. 8.30
Organic Color 200
Turbidity 20
Type Clay . . . . . . Fuller's Earth

Comments

TABLE 6

COAGULATION OF A HIGHLY COLORED SYNTHETIC WATER WITH $MgCO_3$

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	40	117	.5	11.05	56	3.7	-.81	68	96	0										
2	45	120	.5	11.05	46	6.0	-.88	60	96	0										
3	50	122	.5	11.05	45	12.0	-.91	68	80	0										
4	60	128	.5	11.05	34	12.8	-.80	54	72	0										
5	70	134	.5	11.05	31	2.8	-.91	60	72	0										
6	80	140	.5	11.15	23	1.4	-.80	64	72	0	9.0	14	4	46	41	0	41	9		

Characteristics of raw water

Alkalinity as $CaCO_3$ 25
Total Hardness as $CaCO_3$ 25
pH. 8.30
Organic Color 200
Turbidity 60
Type Clay . . . . . . Montmorillonite

Comments

montmorillonite clay turbidity removal is shown.

The use of starch as a flocculant for lime coagulation was studied for both clays. Fifteen experiments were conducted where all system parameters but starch were kept constant. Starch dosages of .2 to 1.6 mg/l were found to reduce the final turbidity in 6 experiments, to have no effect in 6, and to increase the final turbidity in 3. Three experiments were performed with all parameters but the method of starch addition kept constant. The starch was added as a single dose to one jar and in six increments to the second jar as discussed in a previous chapter. The incremental addition increased the efficiency in one test, had no effect in another, and decreased the efficiency in the third. Drew Floc 21, a cationic starch, was used unsuccessfully in one experiment.

Study of Natural Waters

The first natural waters studied were obtained from the Talapoosa River, a source of water for Montgomery, Alabama. Seven sets of jar tests were performed on this water with the results from selected jar tests shown in Table 8. Color and turbidity removal was comparable to alum treatment. The hardness and alkalinity of the magnesium carbonate treated water, 44 mg/l as $CaCO_3$, would allow pH adjustment for corrosion control. This would not be the case for the alum treatment as the alkalinity and hardness were 13 and 22 mg/l respectively. This has led to serious corrosion problems because of the lower buffer capacity.

Water was also obtained from the Mobile River near Mobile, Alabama and evaluated in a similar manner with the selected results for both treatment methods shown in Table 9. It was found that very small dosages of alum were very effective as a flocculant aid. In seven sets of jar tests with alum addition the only variable, a 0.5 mg/l dosage of alum, gave an average of 17% settled color reduction and 50% turbidity reduction as shown in the Table 7.

TABLE 7

EFFECT OF ALUM AS A FLOCCULANT AID IN COLOR AND TURBIDITY COAGULATION WITH MAGNESIUM CARBONATE

Montgomery	$MgCO_3$	pH	Alum	Settled Color	Settled Turbidity
	50	11.30	0	10.8	1.0
	50	11.30	0.5	8.7	0.4
	50	11.30	0.75	9.0	0.5
	45	11.25	0	13	1.6
	45	11.25	0.5	12.5	1.3
	50	11.00	0	15	1.0
	50	11.00	0.5	12	0.2

TABLE 8

$MgCO_3$ AND ALUM COAGULATION OF MONTGOMERY, ALABAMA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	30	125	.5	11.10	15	3.2	-.83	78	52	0										
2	35	130	.5	11.20	10	1.6	-.69	76	56	0										
3	45	125	.5	11.20	12	2.6	-.44	88	56	0										
4	50	115	.5	11.15	9	1.6	-.40	80	60	0	9.0	6	4	40	44	0	44			
5	50	125	.5	11.20	7	1.4	-.35	86	60	0	9.0	5	3	41	44	0	44			
6			20	6.3	6	0.6	+.19	0	0	6	9.0	6	4	9	13	9	22			

Characteristics of raw water

Alkalinity as $CaCO_3$	16
Total Hardness as $CaCO_3$	13
pH.	7.00
Organic Color	50
Turbidity	165
Type Clay	Natural

Comments

TABLE 9

$MgCO_3$ AND ALUM COAGULATION OF MOBILE RIVER WATER, MOBILE, ALABAMA

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	30	130	.5	11.15	10	2.0	-.78	86	48	0										
2	35	130	.5	11.15	10	1.6	-.69	76	56	0										
3	45	115	.5	11.20	13	2.5	-.45	84	56	0								11		
4	45	125	.5	11.25	12	2.6	-.44	88	56	0								10		
5	40	115	.5	11.10	10	2.6		70	50	.0	9.0	9	8	44	52	1	53			
6	0	0	23	7.2	6	2.0	-.55	0	0	33	9.0	8	8	30	38	14	52			

Characteristics of raw water

Alkalinity as $CaCO_3$	42
Total Hardness as $CaCO_3$	42
pH.	6.95
Organic Color	33
Turbidity	39
Type Clay	Natural

Comments

Mobile	$MgCO_3$	pH	Alum	Settled Color	Settled Turbidity
	40	11.00	0	14.5	0.6
	40	11.00	0.25	13.0	0.4
	40	11.00	0.50	13.2	0.3
	40	11.00	1.00	10.0	0
	40	11.00	1.5	11.2	0
	40	10.95	0	18	1.4
	40	10.95	0.5	16	0.6
	40	11.05	0	16.5	1.5
	40	11.05	0.5	12.5	0.6
	40	11.15	0	13.0	1.0
	40	11.15	0.5	10.0	0.6

Alum addition increased the size and rate of floc growth and made the electrophoretic mobility less negative, thereby increasing the Van der Waals attractive forces. A significant linear relationship between mobility and the color or turbidity reduction has been found for most of the waters as will be discussed later.

In the study of waters from cities throughout the country, it was found that many of the waters contained a considerable amount of magnesium. For these waters, lime addition precipitated the magnesium present, requiring no additional magnesium carbonate. In Tables 22 through 37, selected data from these studies are presented. In every case magnesium carbonate gives color and turbidity reductions comparable to alum treatment. The floc formation with magnesium carbonate occurs at a faster rate, the floc formed is larger in size, and settling is more rapid due to the greater floc density. For the waters of high alkalinity and hardness, activated silica was found to be the most effective flocculant aid.

Magnesium present in the natural waters was in most cases in the non-carbonate form. Removal of magnesium as $Mg(OH)_2$ by lime addition will not decrease the total hardness of the stabilized water, merely substitute calcium hardness for magnesium hardness. This can be advantageous in the case of high magnesium waters where the formation of magnesium silicate scales in hot water heaters is a problem.

The raw water analyses, together with the chemical characteristics of the waters following both alum and magnesium carbonate treatment are given for the waters studied in Table 10. For the 17 waters studied, treatment with magnesium carbonate gave a stabilized water with alkalinities ranging from 29 to 55 mg/l as compared with those resulting from alum treatment, which ranged from 9 to 98 mg/l. Values for stabilized hardness ranged from 33 to 83 mg/l as compared with 15 to 136 mg/l for alum treatment. Six of the waters coagulated with alum are too low in hardness and alkalinity to use pH adjustment effectively for corrosion control. In addition, eight waters would benefit by the reduction in total hardness resulting from using magnesium carbonate rather than alum.

TABLE 10

COMPARISON OF THE CHEMICAL CHARACTERISTICS OF 17 RAW AND TREATED NATURAL WATERS

CITY	RAW WATER CHARACTERISTICS					$MgCO_3$ TREATMENT		ALUM TREATMENT	
	Turbidity	Color	Total Alkalinity	Total Hardness	Magnesium as $CaCO_3$	Total Alkalinity	Total Hardness	Total Alkalinity	Total Hardness
Atlanta, Ga.	104	38	11	13	4	38	38	16	18
Baltimore, Md.	2	4	12	40	13	29	53	24	54
Birmingham, Ala.	10	12	74	83	25	40	47	71	87
(a)	15	24	48	71	15	38	56	51	82
Cleveland, Ohio	6	5	92	127	34	36	68	98	136
Detroit, Mich.	3	0	80	100	20	37	57	86	112
Huntsville, Ala(b)	13	4	54	84	13	30	54	52	91
Jackson, Miss.	8	27	10	12	2	39	39	16	23
Lanett, Ala. (c)	105	30	17	17	6	55	55	18	23
Louisville, Ky.	106	11	51	110	33	32	83	59	121
Montgomery, Ala.	165	50	13	16	3	44	44	13	22
Nashville, Tenn.	8	8	71	86	16	32	50	73	97
Opelika, Ala.	14	10	17	17	4	33	33	21	30
Philadelphia, Pa.	41	14	34	69	24	34	66	56	95
Richmond, Va.	24	30	27	43	7	38	53	29	55
Tuscaloosa, Ala.	4	26	4	5	1	40	42	9	15
Washington, D. C.	50	15	41	71	17	40	68	40	76

(a) Requested to be deleted from publication
(b) Tennessee River used for source of raw water
(c) Chattahoochee River used for source of raw water

Solubility of Magnesium Hydroxide

The solubility of magnesium hydroxide has been determined by many investigators. In this study it was increasingly evident that the magnesium remaining in solution after coagulation was many times more than would be predicted by theory. There are several reasons for this apparent increase in solubility. In the jar tests the time allowed for equilibrium was usually only one hour. In plant use, four to six hours are normally allowed for precipitation which should decrease the magnesium solubility. It is the magnesium hydroxide which is precipitated that causes colloidal destabilization and only this portion of the magnesium dosage can be recovered and reused.

The solubility of magnesium hydroxide under jar test conditions varied for each of the natural waters studied. It would have been desirable to determine this solubility relationship for each water, but because of a lack of sufficient data, a composite of 70 observations of magnesium concentrations at varying pH values for all of the waters studied was used. A simple linear regression analysis between log magnesium and pH was used to determine the experimental solubility product, K_{sp}. This value was found to be 1.66×10^{-10} with a standard error of the estimate equal to 1.27.

The solubility relationship found is shown in Figure 6, where the magnesium is plotted as magnesium carbonate tri-hydrate. This composite solubility relationship is used in determining recovery efficiencies and cost estimates for the natural waters studied.

Determination of Conditions for Lowest Treatment Cost

Each water requires a specific amount of magnesium hydroxide for satisfactory treatment. The solubility relationship developed allows calculation of the amount of magnesium carbonate which must be fed to precipitate this amount at various coagulation pH values. For the economic evaluations, three chemical costs will be considered:

1) Dosage of 90% quicklime required to provide the optimum pH

2) Amount of CO_2 required to:
   a) solubilize the $Mg(OH)_2$ in the sludge and
   b) reduce the high pH of the treated water to the pH of stabilization

3) Amount of "make-up" $MgCO_3 \cdot 3H_2O$ to be added.

In addition three alternative conditions are considered:

Case I. Lime recovery is practiced, providing CO_2 at no cost and 90% lime at $.006/lb.

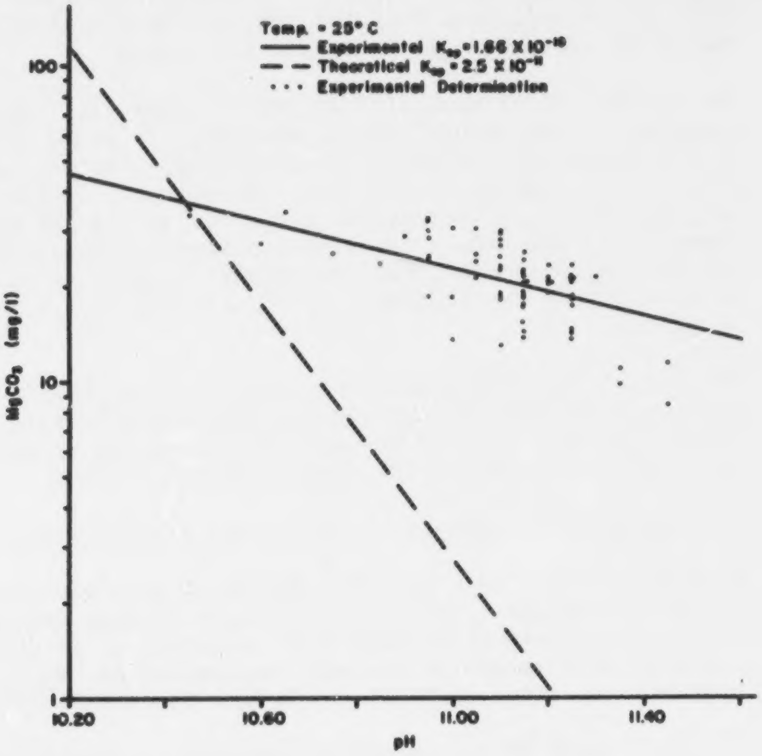


FIG. 6 SOLUBILITY OF $Mg(OH)_2$ (AS $MgCO_3 \cdot 3H_2O$) AS A FUNCTION OF pH FOR 23 NATURAL WATERS

Case II. Lime is purchased at \$.01/lb but CO_2 is available at no cost from a source within or near the water plant.

Case III. Lime is purchased at \$.01/lb and CO_2 generated at a cost of \$.01/lb.

A cost of \$.05/lb was assumed for the $MgCO_3 \cdot 3H_2O$.

A series of curves have been developed that will allow a graphical determination of the pH for coagulation at the least cost. The lime required to increase the pH from 10.5 to some desired value is independent of the total carbonate present in the water. In Figure 7, the cost to raise the pH from 10.5 to the desired pH is shown for the three cases considered. Figure 7 also includes the cost of CO_2 to stabilize the water back to pH 10.5. The $MgCO_3 \cdot 3H_2O$ cost curve was developed from the solubility relationship curve. It was assumed that $MgCO_3 \cdot 3H_2O$ left in solution represented a cost, i.e. make-up coagulant. Summing the magnesium carbonate cost and the lime and CO_2 costs for the three cases, a total cost curve is shown in Figure 8. The optimum pH values and costs can then be determined as:

Case I	pH	=	11.35
	Cost	=	\$9.57
Case II	pH	=	11.15
	Cost	=	\$10.85
Case III	pH	=	11.00
	Cost	=	\$12.45

To this cost, the cost to raise the pH to 10.5 and stabilize the water back to approximately 9.0 must be added. These costs are related to the total alkalinity of the water and are shown in Figure 9 assuming the CO_2 in the water is negligible. Summing the costs in Figures 8 and 9 produces the working curve shown in Figure 10. An additional cost must be added for the lime required to precipitate magnesium hydroxide and for CO_2 used in the recovery process. The costs are shown in Figure 11 and are a function of the amount of $MgCO_3 \cdot 3H_2O$ precipitated. Figures 10 and 11 therefore, represent the two basic working curves for calculating treatment chemical costs.

The total cost found must be reduced by an amount dependent upon the magnesium present in the raw water, as this will reduce the $MgCO_3 \cdot 3H_2O$ make-up. If the coagulation pH results in greater than 100% recovery of $MgCO_3 \cdot 3H_2O$ this value will exceed the cost allocated to the $MgCO_3 \cdot 3H_2O$ remaining in solution as shown in Figure 7. Therefore, before treatment cost estimates are made for a water, using Figure 6, the pH of saturation is determined. When the optimum pH values, determined in Figure 8, are higher than the pH for 100% recovery, the treatment costs are calculated using Figure 8, 9 and 11. The application of these curves will be illustrated using three waters which represent all conditions which might be encountered.

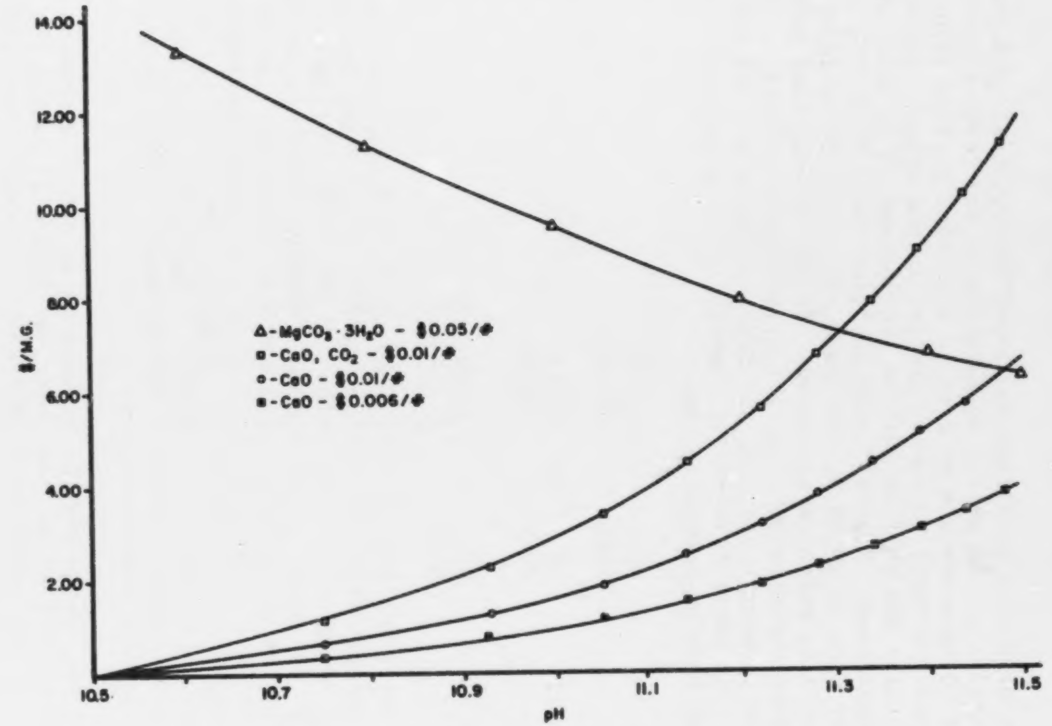


FIG. 7 PARTIAL TREATMENT COSTS IN $/M.G. FOR CaO, CO_2 AND $MgCO_3$ AS A FUNCTION OF COAGULATION pH

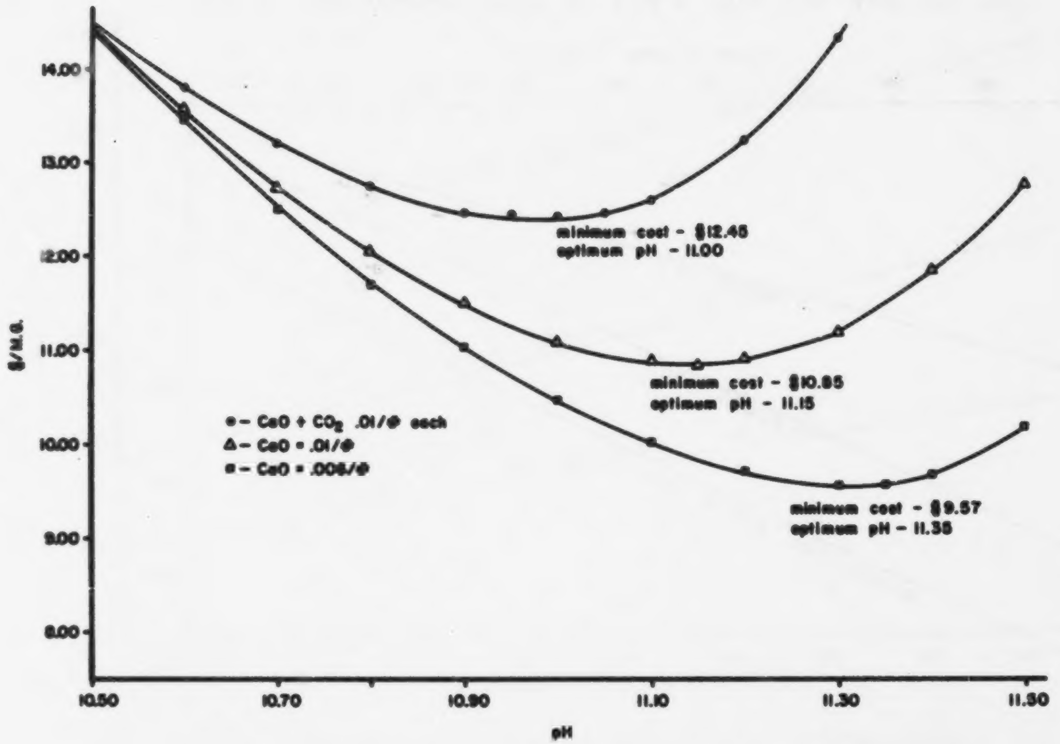


FIG. 8 TREATMENT COST IN $/M.G. AS A FUNCTION OF COAGULATION pH

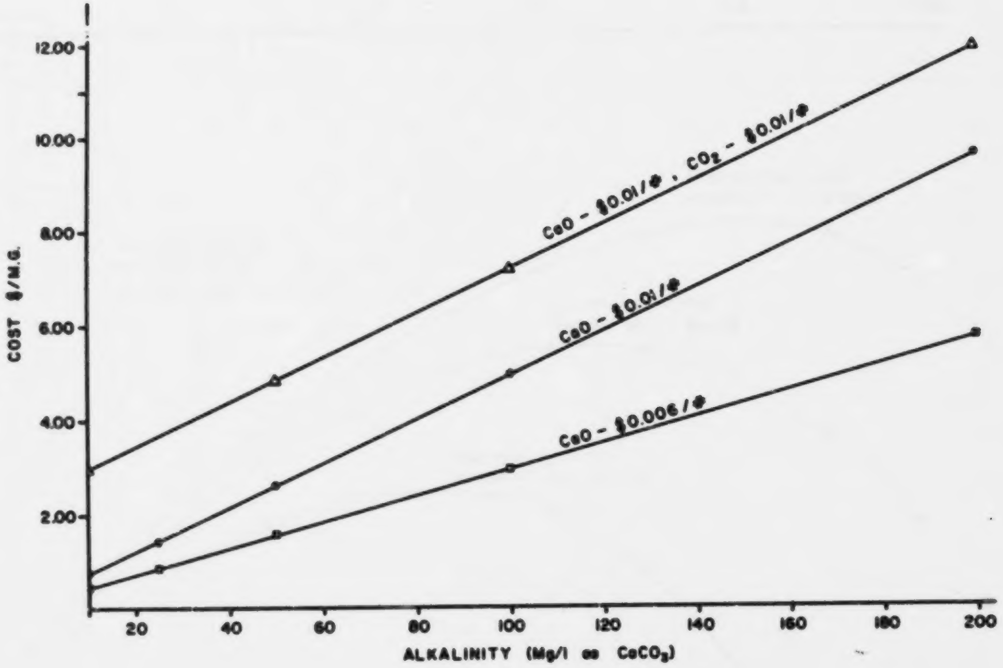


FIG. 9 TREATMENT COST IN $/M.G. FOR CaO AND CO_2 TO RAISE THE RAW WATER pH TO 10.5 AND REDUCE THE pH BACK TO pH 9.0 FOR STABILIZATION

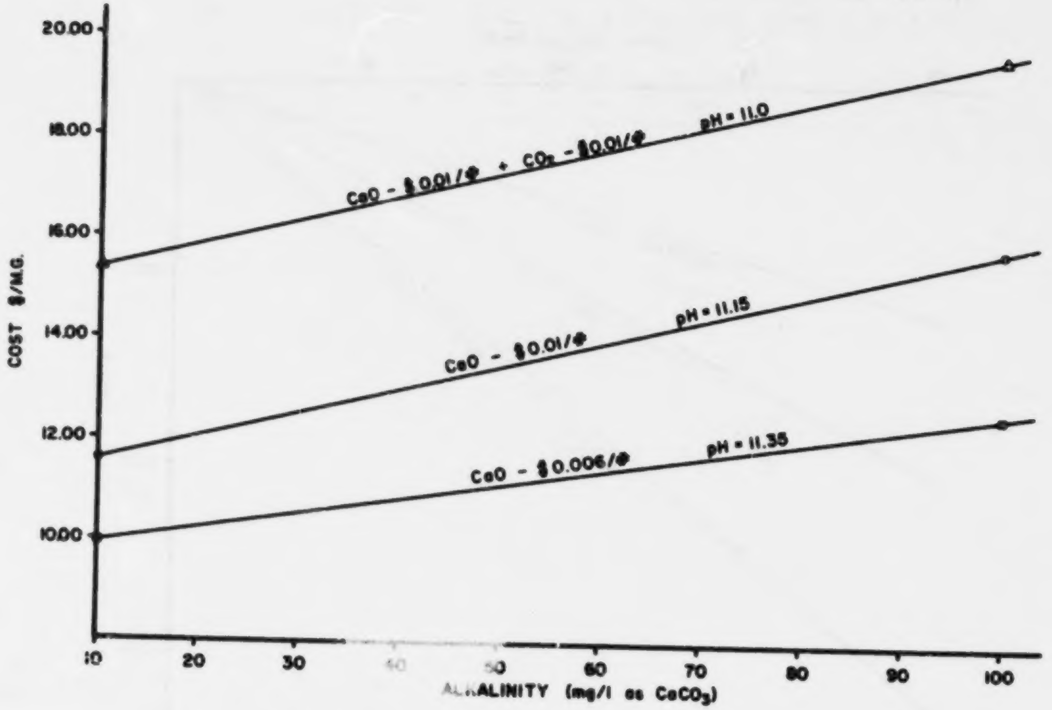


FIG. 10 TREATMENT COST IN $/M.G. AS A FUNCTION OF THE RAW WATER TOTAL ALKALINITY

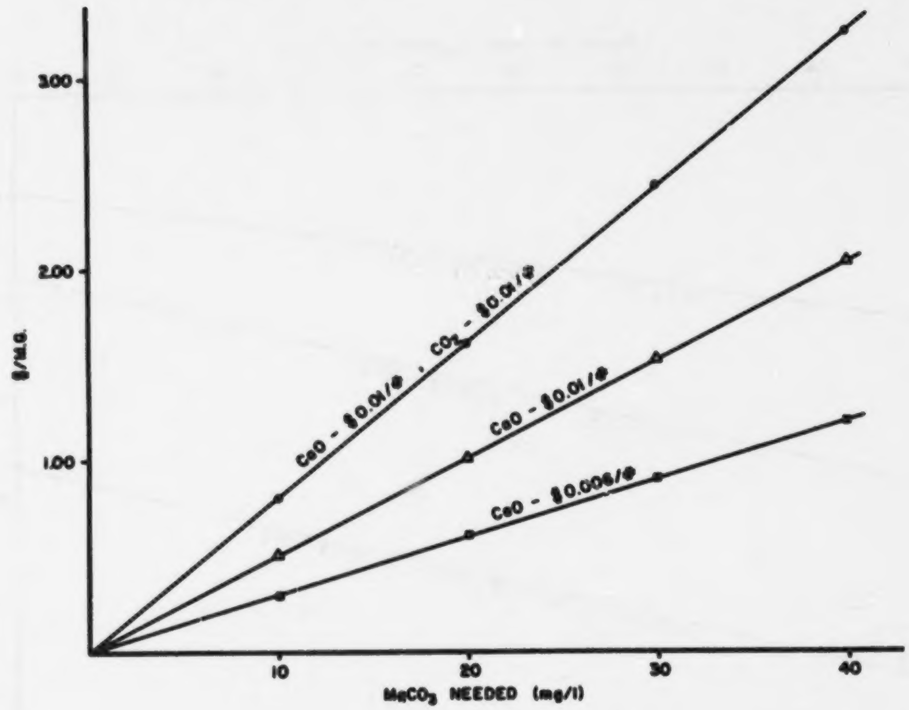


FIG. 11 TREATMENT COST IN $/M.G. AS A FUNCTION OF THE AMOUNT OF $MgCO_3$ PRECIPITATED

Water A - Atlanta, Georgia

Total alkalinity = 11 mg/1
Magnesium (as $MgCO_3 \cdot 3H_2O$) = 5.5 mg/1
Precipitated $MgCO_3 \cdot 3H_2O$ required (from jar test data) = 32 mg/1

This water had a small amount of magnesium present in the raw water. Figure 6 was checked to see that the magnesium recovery was not greater than 100% for the three cases of treatment. The pH value which would represent 100% recovery was greater than 11.6 so the two basic working curves can be used for all cases for this water. From Figures 10 and 11 the costs were calculated as:

	Case I	Case II	Case III
Figure 10 (for a total alkalinity of 11 mg/1)	$10.10	$11.60	$15.38
Figure 11 (for 32 mg/1 $MgCO_3$)	$ 1.02	$ 1.60	$ 2.60
	$11.12	$13.20	$18.00
Credit for magnesium in raw water at $.05/lb for $MgCO_3 \cdot 3H_2O$	$-2.29	$-2.29	$-2.29
	$ 8.73	$10.91	$15.69

Water B - Baltimore, Maryland

Total alkalinity = 12 mg/1
Magnesium as $MgCO_3 \cdot 3H_2O$ = 18 mg/1
Precipitated magnesium carbonate required = 21 mg/1

Figure 6 shows that the pH for 100% recovery is 11.30, which is less than 11.35 used in Case I. Therefore for Case I, an optimum pH of 11.30 will be used. Cases II and III, pH 11.15 and 11.00, would each provide less than 100% recovery so Figures 10 and 11 are used.

	Case I
Cost to raise pH from 10.5 to 11.3 from Figure 7	$ 2.32
Cost to raise pH to 10.5 for an alkalinity of 12 using Figure 9	$ .50
Cost to precipitate 21 mg/1 $MgCO_3 \cdot 3H_2O$ from Figure 11	$ .61
	$ 3.43

	Case II	Case III
Figure 10 (for a total alkalinity of 12 mg/l	$11.65	$15.45
Figure 11 (for 21 mg/l $MgCO_3$)	$ 1.10	$ 1.70
	$12.75	$17.15
Credit magnesium present in water	$-7.50	$-7.50
	$ 5.25	$ 9.65

Water C - Washington, D. C.

Total alkalinity = 41 mg/l
Magnesium as $MgCO_3 \cdot 3H_2O$ present = 23.5 mg/l
Precipitated $MgCO_3 \cdot 3H_2O$ required = 24 mg/l

From Figure 6, the pH for 100% recovery is 10.95. All cases will use this as the pH of coagulation as any pH higher will give greater than 100% recovery.

	Case I	Case II	Case III
Figure 7 (cost to raise pH to 10.95)	$1.30	$2.20	$4.40
Figure 9 (for a total alkalinity of 41 mg/l)	$ .75	$1.25	$1.98
Figure 11 (for 24 mg/l $MgCO_3$)	$ .80	$1.30	$2.50
	$2.85	$4.75	$8.88

This method of determining costs and optimum pH for coagulation is based on the following assumptions:

1) A specific amount of precipitated $Mg(OH)_2$ is required for satisfactory treatment and can be determined by jar testing.

2) The "pooled" magnesium solubility relationship will estimate the actual magnesium solubility in practice. As discussed previously, this is a very conservative estimate and no doubt greater recovery efficiencies will be obtained, allowing a lower optimum operating pH and subsequent cost savings.

3) All relationships are based on the costs shown. If costs are different, the operating pH for the minimum cost will be different.

4) A maximum of 100% recovery of the required $MgCO_3 \cdot 3H_2O$ dosage. It is possible that a stable market for $MgCO_3 \cdot 3H_2O$ will develop which might make it economically attractive to recover greater than 100% of the required $MgCO_3 \cdot 3H_2O$ dosage.

5) Magnesium present in the raw water is an asset and decreases treatment costs.

No credits are given for the savings in chlorine. The costs for the seventeen natural waters studied are calculated and given in Table 11. The present treatment costs shown in this table are for use of only lime and alum and were determined either from laboratory evaluation or annual reports[87-90] supplied by the cities. A recent survey of treatment costs in Alabama[91] was used in cost estimation for the cities in that state. Daily water production was taken from the 1962 Public Health Service Survey[92] where present production was not known.

Electrophoretic Mobility as a Measure of Coagulation Efficiency

The degree to which electrophoretic mobility describes treatment efficiency determines its value as an analytical tool in the coagulation process. A linear regression analysis between particle mobility during coagulation and settled color or turbidity gave an evaluation of this relationship for twelve of the natural waters. Table 12 summarizes the results. In every case, mobility showed a highly significant linear correlation with color reduction. Five of the twelve waters indicated a highly significant linear correlation between mobility and settled turbidity, while two waters were significantly correlated. Figure 12 illustrates the relationship between coagulation particle mobility and settled color for Jackson, Mississippi water. Figure 13 illustrates a high degree of correlation between coagulation particle mobility and settled turbidity for Lanett, Alabama water.

The effect of activated silica on the mobility-turbidity relationship is illustrated for the Cleveland water. A significant relationship existed between particle mobility and residual turbidity for seven coagulation experiments using alum as the flocculant aid. When the five experiments using activated silica as the flocculant aid are included, almost no correlation exists. This effect was noticeable for all jar tests using activated silica. Increased dosages improved the treatment efficiency without reducing the particle mobility.

Charge reversal did not result in a restabilization of the colloidal color nor turbidity as would be expected for alum or ferric sulfate treatment. In Figure 13, turbidity removal increased as the mobility became more positive. In the normal pH range of coagulation with alum, the predominant hydrolysis species is $Al(OH)_3$ which is relatively uncharged.[93] For coagulation with magnesium carbonate, positively charged magnesium hydroxide will predominate at high coagulant dosages. A possible "sweeping effect" of the color or turbidity by the excessive amount of magnesium hydroxide produced could explain the good turbidity removals at highly positive mobilities.

Prediction of the Required Coagulant Dose

Each of the waters required some minimum amount of magnesium hydroxide floc for satisfactory treatment. The amount of $MgCO_3 \cdot 3H_2O$ fed as a coagulant is relatively unimportant since only that portion precipitated as $Mg(OH)_2$ is effective in coagulation. Considering the magnesium

TABLE 11

ECONOMIC COMPARISON OF TREATMENT METHODS FOR 17 NATURAL WATERS

CITY	(b) Avg. Daily Production MGD	(c) $MgCO_3$ Required (mg/l)	Cost in $/M.G. for $MgCO_3$ Treatment and Coagulation pH for Minimum Cost						(g) Present Treatment Costs
			Case 1 (d)		Case 2 (e)		Case 3 (f)		
			Cost	pH	Cost	pH	Cost	pH	
Atlanta, Ga.	65	32	8.73	11.35	10.91	11.15	15.69	11.00	5.94
Baltimore, Md.	211	21	3.43	11.30	5.25	11.15	9.65	11.00	6.08
Birmingham, Ala.	60	15	2.65	10.55	4.45	10.55	7.12	10.55	12.26
(a)	38	22	3.50	11.10	5.82	11.10	10.33	11.00	6.25
Cleveland, Ohio	320	34	3.75	10.50	6.30	10.50	9.45	10.50	5.70
Detroit, Mich.	230	30	3.15	10.50	5.28	10.50	8.30	10.50	6.40
Huntsville, Ala.	10	22	2.80	10.80	4.70	10.80	8.30	10.80	15.00
Jackson, Miss.	21	35	9.89	11.35	12.12	11.15	17.05	11.00	13.50
Lanett, Ala.	4	30	7.59	11.35	10.96	11.15	14.64	10.50	5.00
Louisville, Ky.	84	33	2.27	10.50	3.85	10.50	6.85	11.00	6.12
Montgomery, Ala.	10	40	9.70	11.35	12.23	11.15	18.23	11.00	11.22
Nashville, Tenn.	58	20	3.80	11.00	6.35	11.00	10.30	11.00	5.58
Opelika, Ala.	40	10	8.75	11.35	10.70	11.15	14.75	11.00	6.30
Philadelphia, Pa.	365	24	2.60	10.95	4.35	10.95	6.50	10.95	7.40
Richmond, Va.	32	30	7.37	11.35	8.85	11.15	14.43	11.00	11.08
Tuscaloosa, Ala.	10	10	10.20	11.35	12.00	11.15	16.10	11.00	5.70
Washington, D. C.	167	24	2.85	10.50	4.75	10.50	8.88	10.50	8.39

(a) Requested to be deleted from publication
(b) From 1960 PHS Survey where present production not known
(c) Precipitated $MgCO_3$ as $Mg(OH)_2$
(d) Lime recovery, CaO @ $12.00/ton
(e) CO_2 source available, CaO @ $20.00/ton
(f) CO_2 @ $.01/lb., CaO @ $20.00/ton
(g) Based on annual report supplied by city or laboratory evaluation using alum. Cost includes only lime and alum.

TABLE 12

RELATIONSHIP BETWEEN ELECTROPHORETIC MOBILITIES AND SETTLED COLOR OR TURBIDITY FOR 12 NATURAL WATERS

City	Independent Variable	Observation	Correlation Coefficient	Standard Deviation
Richmond	Color	8	.811**	2.61
Montgomery	Color	33	.811**	5.72
Atlanta	Color	8	.914**	3.57
Jackson	Color	11	.965**	3.23
Tuscaloosa	Color	10	.929**	2.40
Lonett	Color	12	.720**	4.70
Richmond	Turbidity	8	.919**	1.61
Montgomery	Turbidity	33	.757**	4.87
Cleveland	Turbidity	7	.844*	3.18
Cleveland[a]	Turbidity	12	.299	5.24
Atlanta	Turbidity	8	.458	7.62
Jackson	Turbidity	11	.822**	2.36
Birmingham	Turbidity	12	.308	5.11
Philadelphia	Turbidity	8	.824*	1.18
Washington, D.C.	Turbidity	12	.498	2.19
Lonett	Turbidity	12	.852**	1.13
Huntsville	Turbidity	6	.148	3.59
Opelika	Turbidity	6	.919**	2.67
Tuscaloosa	Turbidity	10	.628	1.23

[a] includes data using activated silica

*denotes significant correlation ($\alpha = .05$)

**denotes high significant correlation ($\alpha = .01$)

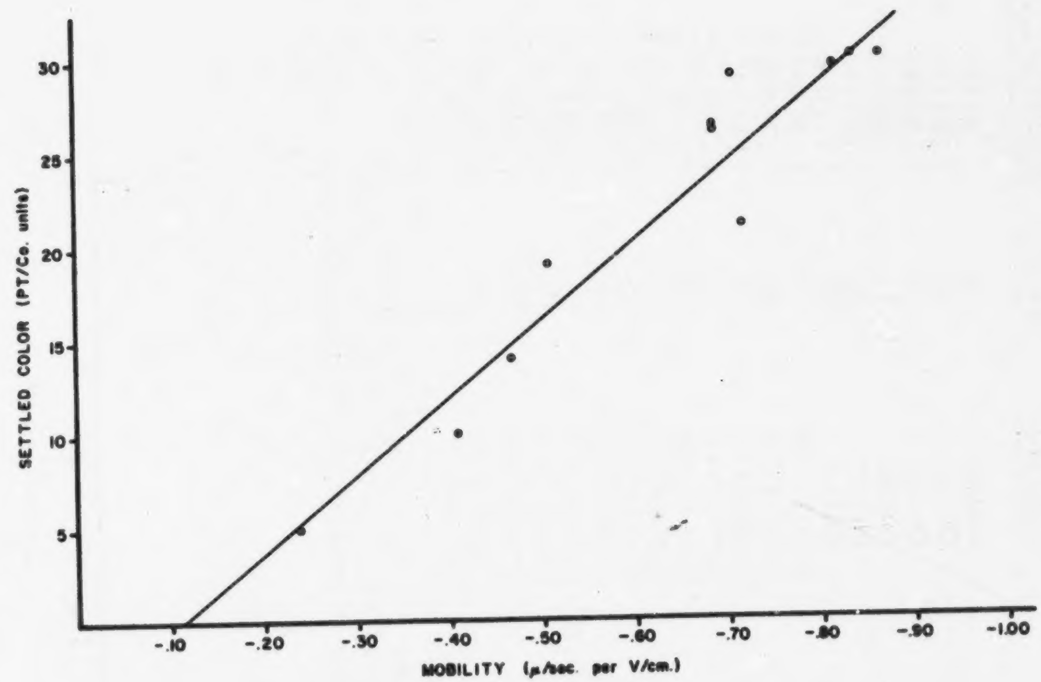


FIG. 12 SETTLED COLOR AS A FUNCTION OF PARTICLE MOBILITY DURING COAGULATION , JACKSON MISSISSIPPI WATER

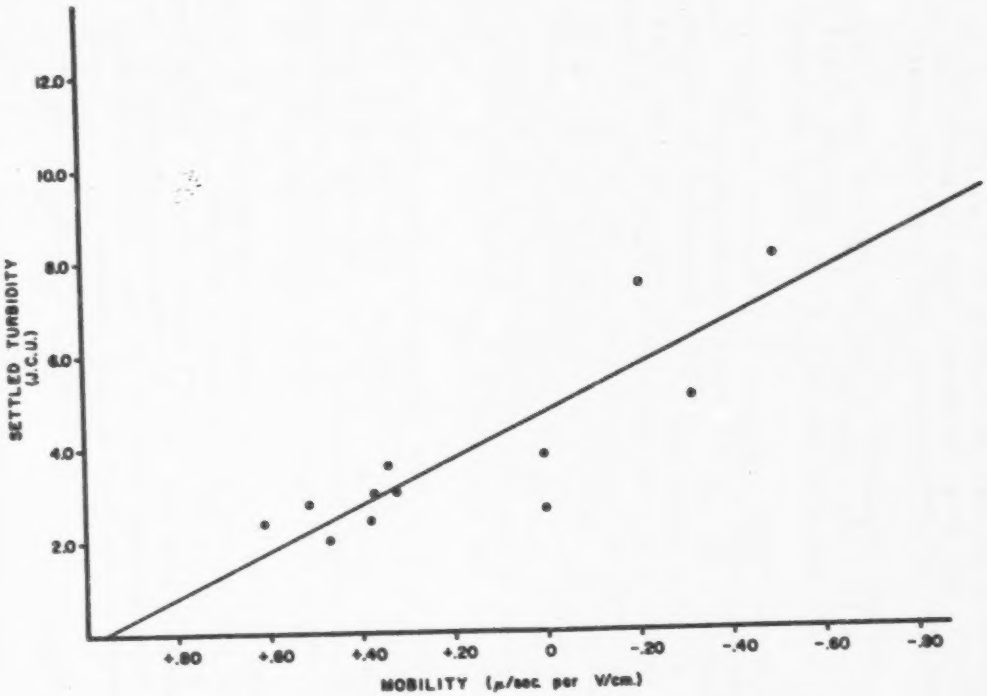


FIG. 13 SETTLED TURBIDITY AS A FUNCTION OF COAGULATION MOBILITY - LANETT WATER

present in the raw water, the magnesium added for coagulation, and the magnesium in solution after coagulation, the magnesium precipitated as $Mg(OH)_2$ can be calculated. The lowest amount of $Mg(OH)_2$ to give satisfactory treatment was determined for each of the seventeen waters.

The required $Mg(OH)_2$ dosage to treat a water must relate to the chemical or physical properties of the water. A stepwise linear regression analysis was made on the data shown in Table 13. The required $Mg(OH)_2$ as $MgCO_3 \cdot 3H_2O$ was regressed as function of a water's color, turbidity, total alkalinity, and total hardness. Again a BMDO2R library computer program[85] was used for the analysis. The resulting equation was:

$$\text{Minimum magnesium dosage (as mg/l of } MgCO_3 \cdot 3H_2O) = 8.33 + .03\,(\text{turbidity}) + .46\,(\text{organic color}) - .03\,(\text{total alkalinity}) + .14\,(\text{total hardness}).$$

The independent variables explained 67.6 percent of variations of the dependent variable, the minimum magnesium dosage, with a standard error of the estimate of 7.1. The variables were added in the order of greatest reduction of the regression sums of squares, i.e., turbidity explained more of the variation of the dependent variable than did hardness. This equation has regression coefficients almost identical to those found for the synthetic waters. While turbidity was significant in explaining relationships, organic color determines the required coagulant dosage. The average color for the seventeen waters studied was only 18. Had it been higher, possibly more statistical significance would have resulted, as was the case for the synthetic waters.

It is interesting to note that neither the base exchange capacity nor the level of turbidity present influenced the coagulant dose to any great extent. Montmorillonite clay, emathlite clay, and natural turbidity each gave similar predictive equations. One hundred JCU of turbidity would require only 2 to 3 mg/l of precipitated $MgCO_3 \cdot 3H_2O$ for coagulation.

Charge reversal did not occur in coagulating emathlite or montmorillonite turbidity. In several synthetic water experiments using kaolinite clay turbidity, a very low, base-exchange capacity clay, charge reversal was common. Possibly charge reversal in natural water coagulation is related to the base exchange capacity of the turbidity present, which could then be a measure of the type of clay present.

Coagulant Recovery

As previously noted, magnesium is separated from softening plant sludge at Dayton by carbonation. The raw water at Dayton is a very clear, hard, ground water with no turbidity or organic color present. Coagulation of turbid waters containing organic color would be a different situation. Turbidity and organic color become highly concentrated in the sludge and would be expected to influence magnesium recovery. Ten experiments, four with natural and six with synthetic waters, evaluated these effects. The results of five of these experiments are shown in

TABLE 13

AMOUNT OF MAGNESIUM PRECIPITATED AS RELATED TO PHYSICAL AND CHEMICAL CHARACTERISTICS FOR 17 NATURAL WATERS

Mg Required (mg/l as $MgCO_3.3H_2O$)	Turbidity (J.C.)	Color (Pt.Co.)	Alkalinity (mg/l)	Hardness (mg/l)
40	165	50	13	16
30	105	30	17	17
10	4	26	4	5
15	10	12	74	83
22	13	4	54	84
10	14	10	17	17
25	106	11	51	110
24	50	15	41	71
30	24	30	27	43
35	7.5	27	10	12
35	6	5	92	127
25	2.5	0	80	100
24	41	14	34	69
32	104	38	11	13
21	2	4	12	40
20	7.5	8	71	86
22	15	24	48	71

Tables 14 through 18. Figure 14, a plot of the values shown in Table 16, graphically demonstrates the relationship between Mg^{++}, Ca^{++}, and color as carbonation proceeds.

Table 19 summarizes the results of the recovery experiments. These experiments show that nearly 100% recovery of magnesium from the sludge was possible. Several experiments indicated greater than 100% recovery of magnesium from the sludge. A combination of analytical error and release of magnesium by the montmorillonite clay on carbonation no doubt accounted for this error. The release of color on carbonation would not be a problem in coagulating waters with an average color of 100 or less. More highly colored waters would require either "wasting" of a portion of the recovered coagulant or a more elaborate recovery process.

In every case the carbonated sludge filtrate was free from turbidity, indicating that release of turbidity would not be a problem. The amount of calcium, as calcium carbonate, released by the sludge on carbonation ranged from 35 mg/l to a high of 200 mg/l. Assuming that the sludge volume was equal to 1% of the total flow, the high value would represent an increase of only 2 mg/l total hardness. The rate of carbonation and the amount of turbidity in the raw water did not appear to effect the solubilization of $Mg(OH)_2$ or the release of color and calcium. Color release was closely related to magnesium solubilization, generally reaching a maximum when about 90% of the magnesium had been recovered.

An interesting aspect of the sludge recovery experiments was the fact that considerably less magnesium was found in solution after coagulation in the 36 liter vessel than in the 1 liter jar tests. The magnesium values found for these studies, at the indicated pH values, are shown in Table 20.

TABLE 20

MAGNESIUM SOLUBILITY AS A FUNCTION OF pH
FOR COAGULANT RECOVERY STUDIES

Mg^{++}(mg/l)	$MgCO_3 \cdot 3H_2O$(mg/l)	pH
1.63	9.4	11.25
0.50	3.3	11.30
0.60	3.4	11.25
0.30	1.7	11.35
0.80	4.5	11.20
1.32	7.5	11.45
0.32	1.8	11.30'
0.11	0.6	11.30
0.65	3.8	11.30

TABLE 14

CARBONATION OF SLUDGE PRODUCED FROM THE COAGULATION OF 36 LITERS OF SYNTHETIC WATER CONTAINING 200 mg/1 OF ORGANIC COLOR AND 50 mg/1 TURBIDITY

Time (Min.)	Mg^{++} (mg/1)	Ca^{++} (mg/1)	Color
1.5	12	18	76
3.0	16	23	138
5.0	14	30	140
10.0	36	28	410
15.0	63	27	440
20.0	105	34	720
30.0	190	40	920
45.0	260	50	1040
60.0	270	40	1020

1460 ml of sludge made up to 2 liters with distilled water.

TABLE 15

CARBONATION OF SLUDGE PRODUCED FROM THE COAGULATION OF 36 LITERS OF SYNTHETIC WATER CONTAINING 200 mg/l ORGANIC COLOR AND 15 mg/l TURBIDITY

Time (Min.)	Mg^{++}(mg/l)	Ca^{++}(mg/l)	Color (Pt.-Co. unit)
5	18	24	85
10	25	30	100
15	52	18	205
20	86	28	370
30	130	54	480
45	184	30	760
60	212	34	820
75	218	37	1080
90	248	48	1180
100	255	48	1180
110	265		1020

1360 ml of sludge made up to 2 liters with distilled water.

TABLE 16

CARBONATION OF SLUDGE PRODUCED FROM THE COAGULATION OF 36 LITERS OF SYNTHETIC WATER CONTAINING 50 mg/l ORGANIC COLOR AND 15 mg/l TURBIDITY

Time (min.)	pH	Mg^{++}(mg/l)	Ca^{++}(mg/l)	Organic Color (Pt.Co. units)
5		17	22	100
10	8.35	26	25	138
15	7.75	32	25	165
20	7.35	40	30	146
25	7.00	45	40	214
30	6.85	48	50	130
45	6.70	52	65	146

1300 ml sludge made up to 2 l with distilled water before carbonation.

TABLE 17

CARBONATION OF SLUDGE PRODUCED FROM THE COAGULATION OF 36 LITERS OF SYNTHETIC WATER CONTAINING 15 mg/l ORGANIC COLOR AND 15 mg/l TURBIDITY

Time (Min.)	pH	Mg^{++}(mg/l)	Ca^{++}(mg/l)	Color (Pt.Co. units)
5	9.20	6	25	12
10	7.20	16	29	15
15	6.85	26	54	32
20	6.60	25	66	50
25	6.60	27	94	30
40	6.50	30	108	32

1375 ml of sludge made up to 2 liter volume.

TABLE 18

CARBONATION OF SLUDGE PRODUCED FROM THE COAGULATION OF 36 LITERS OF NATURAL WATER CONTAINING 200 mg/l OF ORGANIC COLOR AND 50 mg/l ADDED MONTMORILLONITE CLAY TURBIDITY

Time (Min.)	pH	Mg^{++}(mg/l)	Ca^{++}(mg/l)	Color (Pt.Co. units)
5	--	13	33	40
10	--	35	28	165
15	9.35	54	32	240
20	8.90	76	31	360
30	7.20	112	46	410
40	6.85	119	48	545

Total sludge volume 2820 ml. 1410 ml made up to 2 l for this experiment.

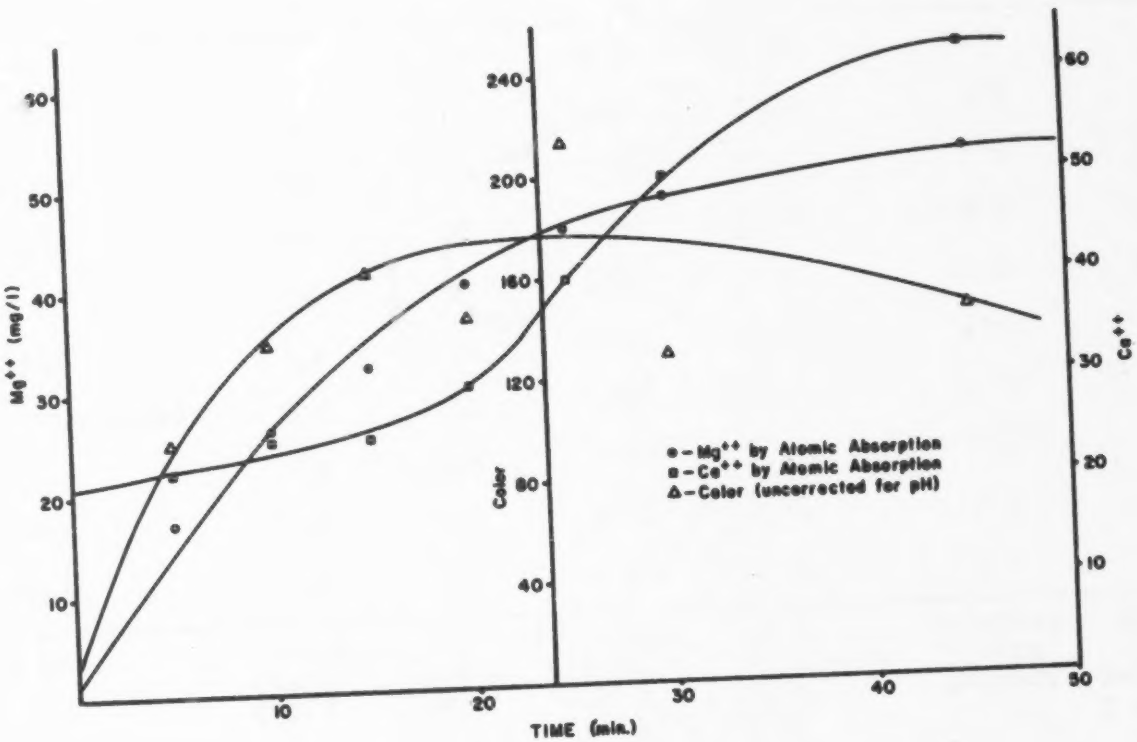


FIG. 14 MAGNESIUM RECOVERY BY CARBONATION

TABLE 19

COAGULANT RECOVERY STUDIES

Water	Color (Pt.Co. units)	Tur-bidity (J.C.)	$MgCO_3 \cdot 3H_2O$ Added (Grams)	$MgCO_3 \cdot 3H_2O$ in Sludge (Grams)	Percent Color Released	% $MgCO_3$ Recovered From Sludge
Montgomery	50	165	0.15	0.07	11.0	45
Montgomery	50	165	0.45	0.25	4.5	54
Atlanta	38	104	1.26	1.15	4.2	92
Austin Cary Forest	200	50	2.80	2.70	25.0	96
Synthetic	15	50	0.53	0.38	6.1	73
Synthetic	50	50	1.40	1.41	18.0	100
Synthetic	200	50	2.88	3.00	28.0	106
Synthetic	200	15	2.88	3.00	16.0	103
Synthetic	50	15	0.72	0.59	9.0	83
Synthetic	15	15	0.36	0.34	25.0	95

This could have been due to a mass action effect increasing the $Mg(OH)_2$ precipitation rate. However the longer time allowed for settling, from 3 to 12 hours, is a more likely explanation. Both effects would be present in actual plant conditions tending to make the economic evaluation, based on higher magnesium solubility, more conservative.

Limited studies of sludge filterability showed that the carbonated sludge was considerably easier to filter than the uncarbonated sludge. Treatment of the carbonated sludge with 1.5 mg/l of anionic polymer increased the filterability while higher dosages tended to have a negative effect. Approximately 1 g/l of $CaCO_3$ greatly improved filterability producing a dry, friable cake. Indications are that only sludges produced in treating very soft waters will present any problem in dewatering. Addition of an inert material, such as $CaCO_3$, or the use of polymers may be necessary for these waters. The $CaCO_3$ precipitated in stabilization may be adequate for this purpose.

Coagulation With Recovered Magnesium

Table 21 demonstrates the effectiveness of recovered magnesium. Three levels of magnesium carbonate were used to determine the effectiveness of twice-recovered magnesium bicarbonate in solution. This magnesium had been used twice in previous experiments. The resulting settled color, turbidity, stabilized chemical characteristics of water so treated were almost identical with those of water treated with fresh material. The reused magnesium bicarbonate was that recovered from treating a highly colored water, thus representing the most unfavorable conditions.

Application of the Process

The use of this new coagulation process in large water treatment plants allows the recovery and reuse of both the lime and the magnesium carbonate with carbon dioxide supplied from the recalcination of the lime.

The majority of the more than 4000 water plants in the United States however, will not find it economically attractive to recover lime. Since the CO_2 produced in recalcination greatly reduces the treatment cost, it would be advantageous to locate an inexpensive source near the plant. In many cases such a source exists in the form of diesel or natural gas engine exhaust, stack gases from incinerators or power plants, or some other industrial source. As noted in Table 11, the difference in treatment costs between Cases II and III is due entirely to the purchase of CO_2.

A flow diagram of the unit operations involved is shown in Figure 15. The sludge from the settling basin, containing $Mg(OH)_2$, $CaCO_3$, turbidity, color, etc., is pumped to the carbonation tank. Carbon dioxide is introduced with rapid mixing for a detention time of approximately one hour. The magnesium is completely solubilized as $Mg(HCO_3)_2$ or $MgCO_3$ while the $CaCO_3$, turbidity, etc. remain as solids. Vacuum filtration separates the solids so that the liquid phase, containing the magnesium,

TABLE 21

EVALUATION OF TWICE RECYCLED MAGNESIUM IN COAGULATION OF SYNTHETIC WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
*1	40	130	.5	11.15	36	4	-.62	82	96	0										
*2	50	142	.5	11.15	34	8	-.61	60	92	0										
*3	60	153	.5	11.10	33	5	-.71	50	84	0	9.0	20	6	44	41	0	41	4		
4	40	112	.5	11.15	34	6	-.62	68	100	0										
5	50	117	.5	11.00	41	8	-.70	46	100	0										
6	60	122	.5	11.15	30	12	-.67	70	76	0	8.7	18	0	49	47	0	47	6		

Characteristics of raw water

Alkalinity as $CaCO_3$ 25
Total Hardness as $CaCO_3$ 25
pH. . . . .
Organic Color 110
Turbidity 60
Type Clay . . . . . . Montmorillonite

Comments

*Twice recovered solution of $Mg(HCO_3)_2$ used as coagulant

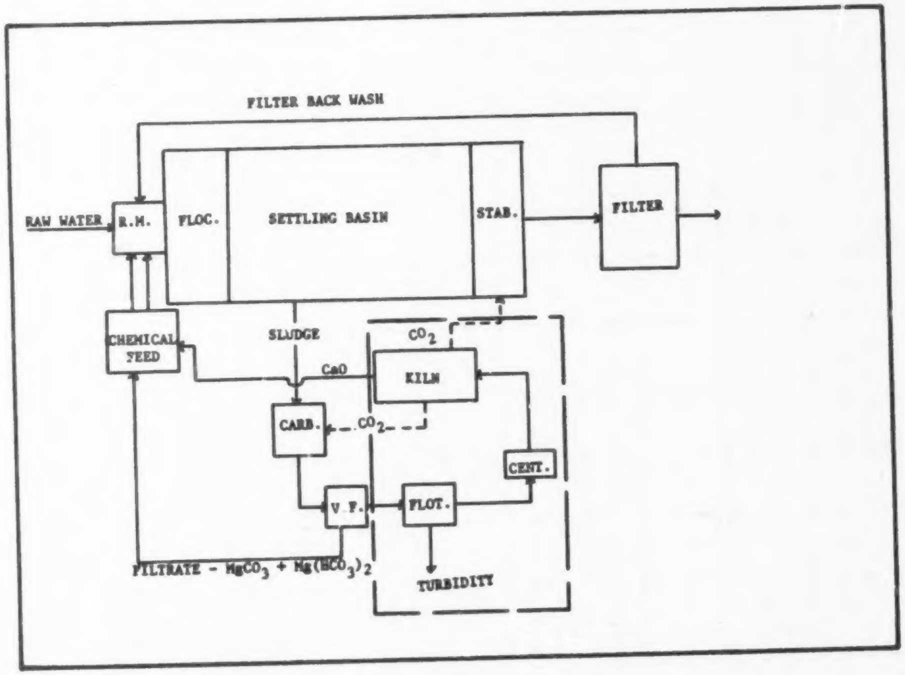

FILTER BACK WASH
RAW WATER
R.M.
FLOC.
SETTLING BASIN
STAB.
FILTER
CHEMICAL FEED
SLUDGE
CaO
CO_2
KILN
CARB.
CO_2
CENT.
V.F.
FLOT.
FILTRATE - $MgCO_3$ + $Mg(HCO_3)_2$
TURBIDITY

FIG. 15 FLOW DIAGRAM FOR TURBIDITY REMOVAL PLANT USING $MgCO_3$ AND LIME RECALCINING

can be recycled for reuse. If lime is not recovered, this filter cake represents a plant waste which could be handled easily and disposed of as land fill or it might find application in agricultural use as a pH stabilizer for soil. Carbon dioxide, from either a source available near the plant or by generation, is supplied to the carbonation and stabilization units.

The dashed lines in Figure 15 show the additional unit operations necessary for lime recovery. The filter cake is slurried and the clay turbidity, color, etc. floated off in a small flotation cell. This process, which has been shown to be successful at a very minimal cost, purifies the calcium carbonate before recovery. The small volume of float, which can easily be dewatered and disposed of as land fill, represents the only waste product from the entire process. The relatively pure calcium carbonate is then dewatered by centrifugation, and burned in a lime kiln producing calcium oxide and carbon dioxide. The calcium oxide is then slaked and reused while the carbon dioxide is used for stabilization of the water and carbonation of the sludge as shown in the flow diagram.

Sludge thickening before carbonation could prove to be desirable. For most waters, the sludge before carbonation will rarely exceed 1% solids, suspended in water containing 70-80 mg/l of hydroxide alkalinity. Thickening the sludge to 3% solids would allow recycling of the clear, highly alkaline supernatant which would have a volume equal to 2/3 of the total sludge flow. This would reduce the required lime dosage and also reduce the amount of carbon dioxide required for sludge carbonation as well as the size of the carbonation basin. These advantages must be weighed against the capital cost and operational problems resulting from the additional unit required.

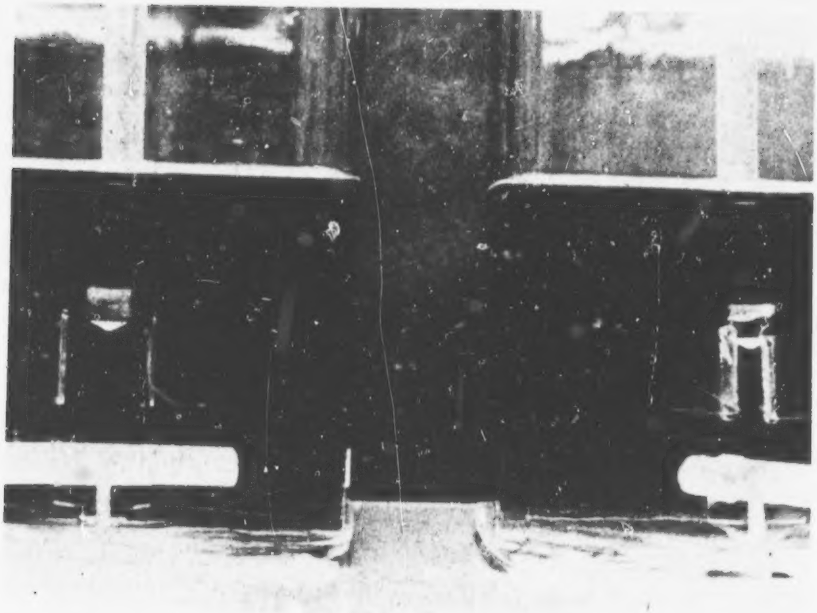
Plants reusing lime must carbonate sludge on a continuous basis. For a one hour carbonation detention time, a fifty million gallon per day plant would require only an 11,000 gallon carbonation basin, assuming the sludge volume is 0.5% of the total flow. A five million gallon per day plant, recovering magnesium on a batch basis, would require a 25,000 gallon basin for the same conditions. In addition, at least a 25,000 gallon storage tank for the magnesium carbonate solution would be necessary. Sludge thickening prior to carbonation would reduce the size of both tanks.

Where lime recovery is not practiced, plants treating a moderately turbid water could vacuum filter the carbonated sludge on an intermittent basis. All of the carbonated sludge could be recycled until the solids reached an undesirable level. Removal of the solids by vacuum filtration would allow the cycle to continue. The increased solids concentration could possibly increase the coagulation and settling efficiency, particularly for waters very low in turbidity.

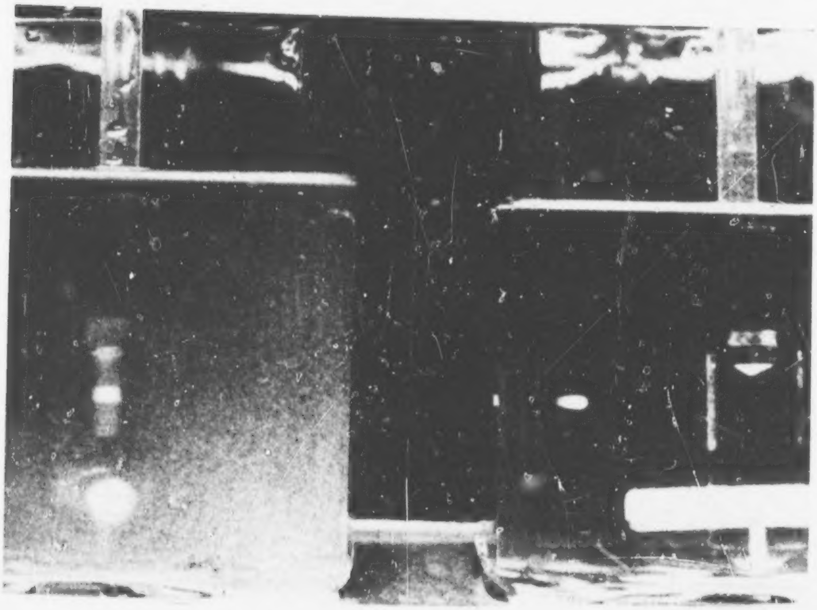
Photographic Comparison of the Formation of Flocs Produced With Magnesium Carbonate and With Alum

In all of the coagulation studies, the magnesium carbonate flocs formed more rapidly and were generally larger in size and more dense than the alum flocs. Photographs taken during coagulation of organic color with alum in one jar and with $MgCO_3$ in the other allow comparison of both the rate of floc formation and the physical characteristics of the two flocs formed. The raw water which was coagulated contained 250 mg/l of organic color with an adjusted alkalinity and hardness of 30 mg/l. The dosage of alum required for good coagulation was established as 85 mg/l. The optimum dosage of $MgCO_3$ was 140 mg/l, hydrolyzed with 160 mg/l of hydrated lime. A dosage of 0.5 mg/l of potato starch was used as a flocculant with the magnesium carbonate treatment. Five minutes of rapid mixing, fifteen minutes of slow mixing, and twenty minutes' settling was provided as in previous jar tests.

Figure 16 shows the water before addition of coagulants and five minutes after the coagulants were added. Figure 17 shows the floc formed seven minutes after coagulant addition.



Before coagulant addition



Five minutes after coagulant addition

FIG. 16 PHOTOGRAPHIX COMPARISON OF $MgCO_3$ AND ALUM FLOC DURING RAPID MIXING IN THE REMOVAL OF ORGANIC COLOR

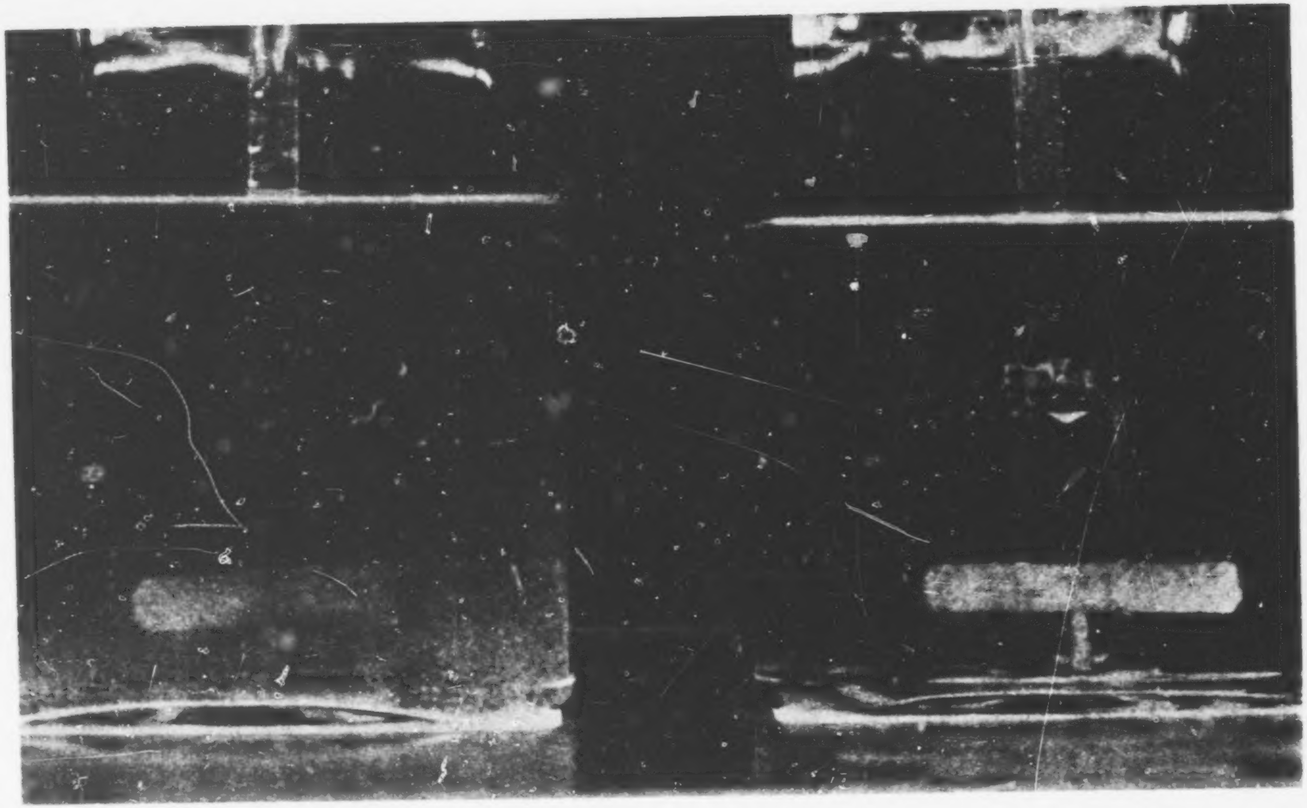


FIG. 17 PHOTOGRAPHIC COMPARISON OF $MgCO_3$ AND ALUM FLOC DURING FLOCCULATION IN THE REMOVAL OF ORGANIC COLOR

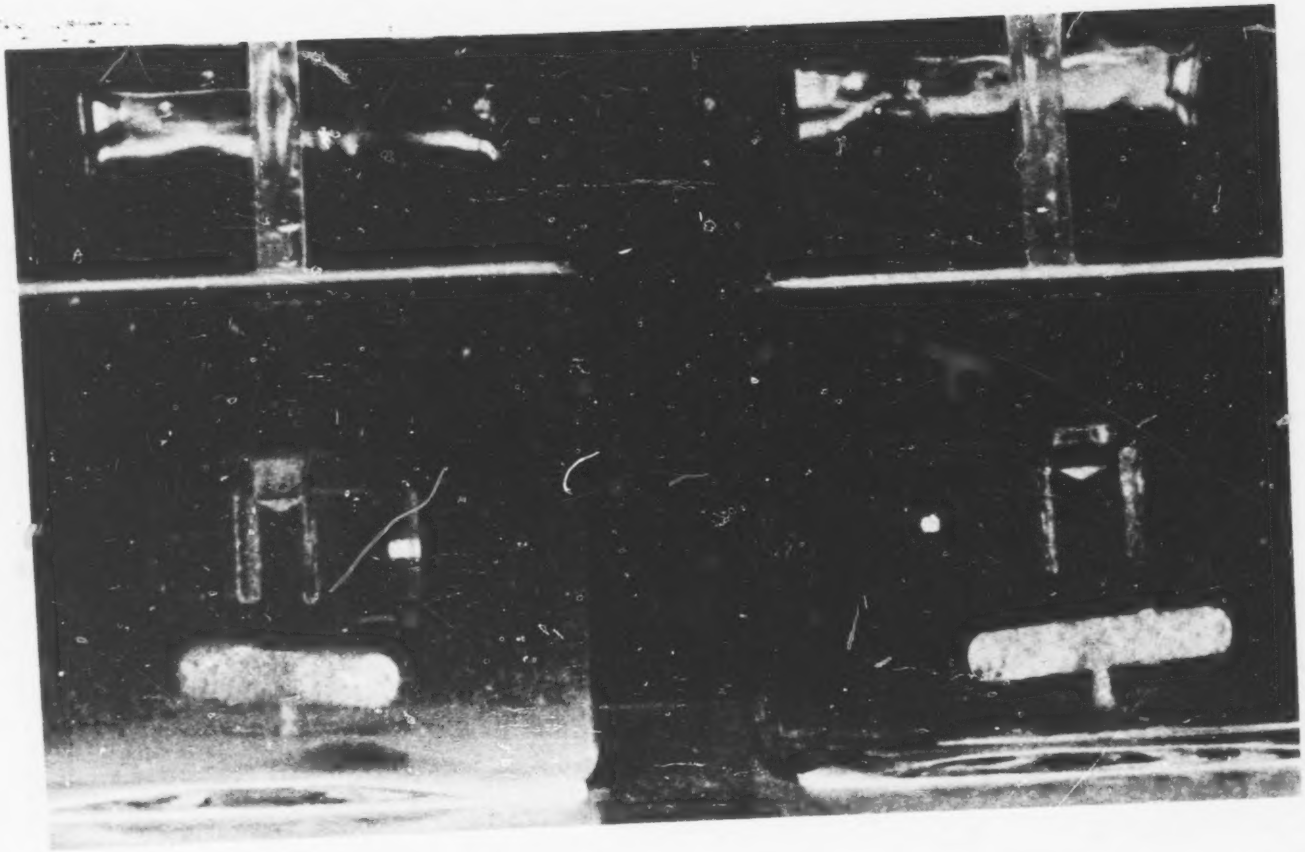


FIG. 18 PHOTOGRAPHIC COMPARISON OF THE RATE OF SETTLING FOR $MgCO_3$ AND ALUM FLOCS FORMED IN THE REMOVAL OF ORGANIC COLOR

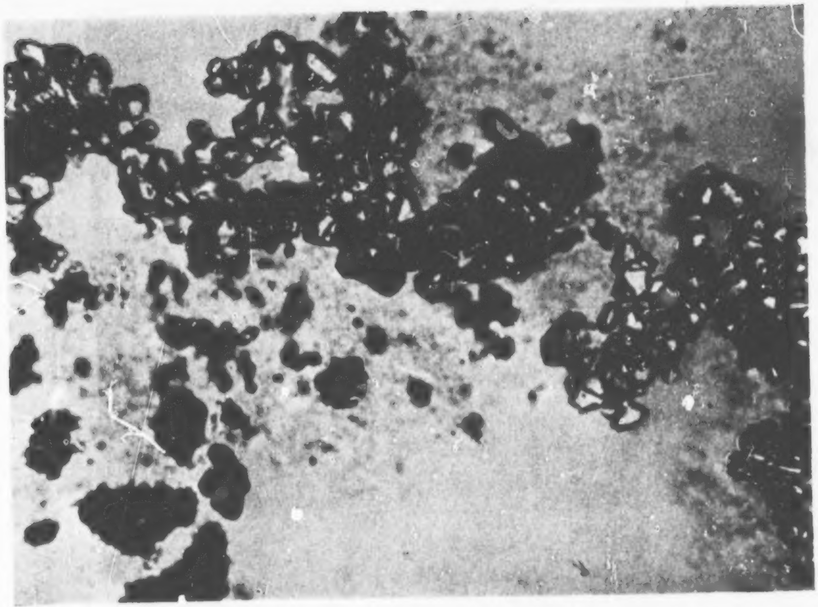


FIG. 19 MAGNESIUM CARBON FLOC (MAGNESIUM HYDROXIDE DARK WITH ABSORBED COLOR AND CALCIUM CARBONATE CRYSTALS) MAGNIFIED 200 TIMES

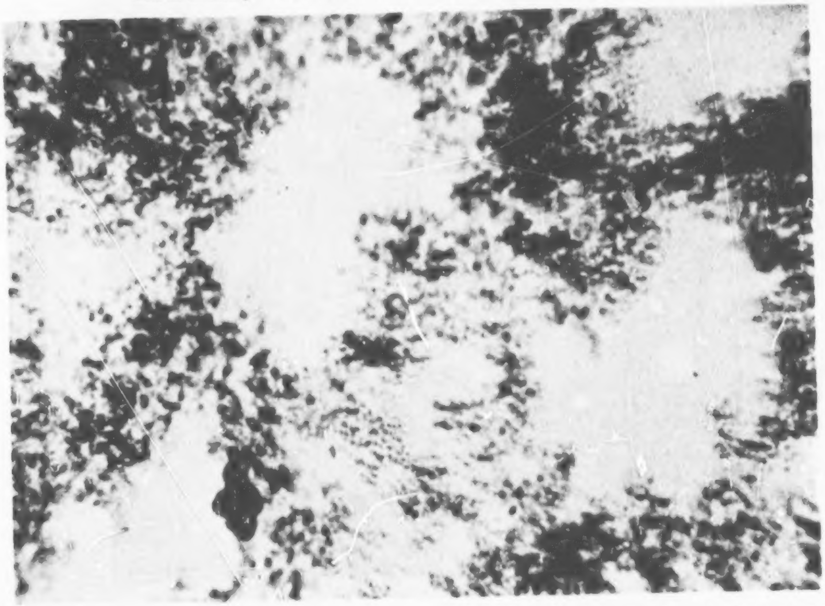


FIG. 20 PHOTO-MICROGRAPH OF ALUM FLOC MAGNIFIED 100 TIMES

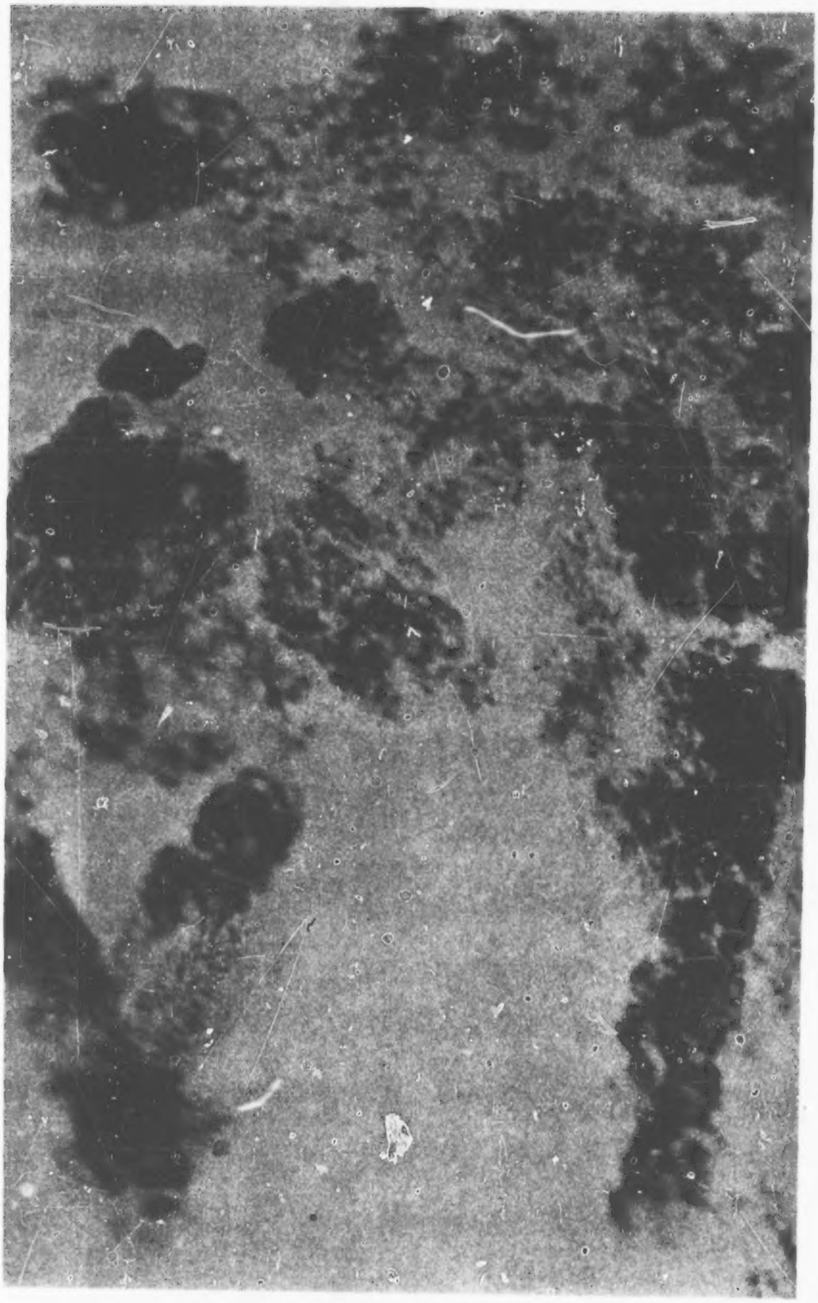


FIG. 21 PHOTO-MICROGRAPH OF ALUM FLOC MAGNIFIED 200 TIMES

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SECTION IX. APPENDIX

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TABLE 22

COAGULATION OF ATLANTA, GEORGIA WATER WITH $MgCO_3$ AND ALUM

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	20	91	.5	11.15	24	23.0	-.45	64	60	0										
2	30	97	.5	11.15	20	14.0	-.34	76	64	0										
3	40	103	.5	11.15	15	4.6	0	68	76	0	9.0	11	0	45	45	0	45	16		
4	40	118	.5	11.25	2	1.0	+.41	92	60	0	9.0		0	38	38	0	38	10		
5			10	7.50	9	6.0		0	0	10										
6			13	7.48	8	3.0		0	0	8	9.0		0	16	16	2	18			

Characteristics of raw water

Alkalinity as $CaCO_3$ 11
Total Hardness as $CaCO_3$ 13
pH. 7.65
Organic Color 38
Turbidity 104
Type Clay . . . . . . Natural
Magnesium as $CaCO_3$ 4

Comments

Raw water mobility -1.24

TABLE 23

$MgCO_3$ AND ALUM COAGULATION OF BALTIMORE, MARYLAND WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	--	95	2	11.15		2.1	-.57	74	48	0	9.0		0	54	54	32	86	10		
2	15	105	1.5	11.15		3.5	-.47	70	60	0										
3	20	105	.5	11.15		2.5	-.33	64	56	0										
4	25	107	.5	11.15		2.1	0	56	60	0	9.0		0	40	40	29	69	16		
5			8	6.00		1.3		0	0	10	9.0		-	24	24	30	54			
6			10	6.00		0.6														

Characteristics of raw water

Alkalinity as $CaCO_3$ 12
Total Hardness as $CaCO_3$ 40
pH. 6.00
Organic Color 4
Turbidity 2
Type Clay . . . . . . Natural
Magnesium as $CaCO_3$ 13

Comments

TABLE 24

LIME AND ALUM COAGULATION OF BIRMINGHAM, ALABAMA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Ca $(OH)_2$	Alum	Ha 196					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	90	.5		10.70	8	15	-.55	45	70	0										
2	130	.5		11.15	7	4.5	-.58	72	48	0	9.0	3	2	37	39	5	44	14		
3	140			11.18	8	5.5	-.58	80	48	0										
4	150		.5	11.25	8	4.6	0	81	62	0	9.0	3	0	52	52	9	61	18		
5		15		7.50	8	1.0		0	0	62										
6		20		7.45	6	0		0	0	60	8.8	7	8	63	71	16	87	25		

Characteristics of raw water

Alkalinity as $CaCO_3$ 74
Total Hardness as $CaCO_3$ 83
pH. 7.60
Organic Color 12
Turbidity 10
Type Clay . . . . . . Natural
Magnesium as $CaCO_3$ 25

Comments

Raw water mobility -.77

TABLE 25

$MgCO_3$, LIME, AND ALUM COAGULATION OF CHATTANOOGA, TENNESSEE WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$MgCO_3$	$Ca(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1		120	.5	11.15	19	15	-.81	86	56	0	9.0	6	0	42	42	20	62	11		
2	15	116	.5	11.10	15	10	-.42	64	60	0	9.0	6	0	38	38	18	56	13		
3	20	125	.5	11.15	15	10	0	86	68	0										
4	25	128	.5	11.15	11	7	+.38	82	72	0	9.0	4	0	44	44	22	66	16		
5			15	7.30	11	3.0		0	0	40										
6			20	7.25	8	1.8		0	0	38	9.0	7.0	0	51	51	31	82	15		

Characteristics of raw water

Alkalinity as $CaCO_3$ 48

Total Hardness as $CaCO_3$ 71

pH. 7.85

Organic Color 24

Turbidity 15

Type Clay . . . . . . Natural

Magnesium as $CaCO_3$ 15

Comments

Mobility of raw water -1.07

TABLE 26

COAGULATION OF CLEVELAND, OHIO WATER WITH LIME AND ALUM

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$Ca(OH)_2$	$=SiO_2=$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	90	2.0		10.35	2	4.8	-1.10	14	44	0	9.0	1	0	39	39	31	70	27		
2	90	4.0		10.35	2	3.3	-1.02	14	50	0	9.0	1	0	47	47	32	79	27		
3	160			11.20	2	6.0	0	76	28	0	9.0		0	38	38	32	70	13		
4	180		.5	11.35	2	2.7	+.57	88	28	0	9.0		0	36	36	32	70	9		
5			8	7.90	2	4.0		0	0	88										
6			10	7.80	2	2.6		0	0	86	9.0		0	98	98	38	136			

Characteristics of raw water

Alkalinity as $CaCO_3$	92
Total Hardness as $CaCO_3$	127
pH.	8.10
Organic Color	5
Turbidity	6
Type Clay	Natural
Magnesium as $CaCO_3$	34

Comments

TABLE 27

COAGULATION OF DETROIT, MICHIGAN WATER BY PRECIPITATION OF MAGNESIUM PRESENT BY LIME ADDITION

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$Ca(OH)_2$	Alum	$=SiO_2=$					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	75		4.0	10.70		3.5		14	38	0										
2	40		1.0	10.50		5.5		2	56	0	9.0		0	42	42	31	73			
3	120		3.0	11.10		9.0	-.34	50	28	0										
4	120			11.10		6.0	-.53				9.0		0	37	37	20	57	20		
5	150	.5		11.20		5.0	-.46	74	24	0	9.0		0	35	35	17	52	9		
6		15		7.60		2.0		0	0	74	9.0		0	86	86	26	112	30		

Characteristics of raw water

Alkalinity as $CaCO_3$ 80
Total Hardness as $CaCO_3$ 100
pH. 7.90
Organic Color 0
Turbidity 2.5
Type Clay . . . . . . Natural
Magnesium as $CaCO_3$ 30

Comments

TABLE 28

COAGULATION OF HUNTSVILLE, ALABAMA WATER WITH $MgCO_3$ AND WITH ALUM

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$	Calcium as $CaCO_3$	
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	0	0	7	7.5	5.0	3.0	-.48	0	0	50	9.0		6	52	58	33	91	20	71	
2	15	120	.5	11.15	3.0	3.8	-.37	88	48	0										
3	20	125	.5	11.15	1.0	2.5	0	92	60	0	9.0		2	28	30	24	54	14	40	
*4	20	125	.5	11.15	3.0	6.4	-.56	86	64	0										
5	20	110	.5	10.95	1.0	10.0	+.48	54	44	.0								31		
6	30	115	.5	11.05	1.0	10.0	0	62	44	0								24		

Characteristics of raw water

Alkalinity as $CaCO_3$	54
Total Hardness as $CaCO_3$	84
pH.	7.5
Organic Color	4
Turbidity	13
Type Clay	Natural

Comments

*Ha195 at .5 mg/1

TABLE 29

$MgCO_3$ AND ALUM COAGULATION OF JACKSON, MISSISSIPPI WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$MgCO_3$	$Ca(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	20	90	.5	11.10	30	9.3	-.84	74	52	0										
2	30	95	.5	11.10	27	7.7	-.69	66	64	0										
3	40	113	.5	11.20	13	1.6	-.51	78	68	0										
4	50	119	.5	11.15	5	2.4	-.24	74	56	0	9.0	5	2	38	39	0	39	11		
5			20	6.80	12	0		0	0	.9										
6			25	6.60	7	0		0	0	8	9.0	8	0	16	16	7	23			

Characteristics of raw water	
Alkalinity as $CaCO_3$	10
Total Hardness as $CaCO_3$	12
pH.	7.55
Organic Color	27
Turbidity	7.4
Type Clay	Natural
Magnesium as $CaCO_3$	2

Comments

TABLE 30

$MgCO_3$ AND ALUM COAGULATION OF LANETT, ALABAMA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$MgCO_3$	$Ca(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	30	105	.5	11.15	30	5.0	-.32													
2	35	108	.5	11.15	13	3.0	+.37													
3	40	110	.5	11.15	11	2.0	+.47	94	60	0								14		
4	35	125	.5	11.25	13	2.4	+.34	87	54	0	9.0	4	0	53	53	8	61	13		
5			10	7.10	13	3.6		0	0	.7	9.0	5.0	2	16	18	5	23			
6			15	7.00	11	3.6		0	0	5	9.0	5.0	2	12	14	9	25			

Characteristics of raw water

Alkalinity as $CaCO_3$	17
Total Hardness as $CaCO_3$	17
pH.	7.55
Organic Color	30
Turbidity	105
Type Clay	Natural

Comments

TABLE 31

LIME AND ALUM COAGULATION OF LOUISVILLE, KENTUCKY WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$Ca(OH)_2$	Alum	$SiO_2^{=}$					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	60		2.0	10.75	3	14.5		34	60	0										
2	120		2.0	11.20	3	8.0		92	60	0										
3	100	.5		10.90	10	7.8	+.38	42	60	0	9.0	5	0	32	32	61	83	17		
4	140	.5		11.25	4	4.5	+.73	80	56	0	9.0	4	0	28	28	55	81	12		
5		10		7.35	6	1.8		0	0	50	9.0	5	0	59	59	62	121			
6		15		7.30	4	1.4		0	0	48										

Characteristics of raw water

Alkalinity as $CaCO_3$ 51

Total Hardness as $CaCO_3$ 110

pH. 7.50

Organic Color 11

Turbidity 106

Type Clay . . . . . . Natural

Magnesium as $CaCO_3$ 33

Comments

Mobility of raw water -.98

TABLE 32

$MgCO_3$, LIME, AND ALUM COAGULATION OF NASHVILLE, TENNESSEE WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$	Stabalized Turbidity	
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1		110	.5	10.95	8	5.4	-.63	43	54	0	9.0	8	2	40	42	16	58	15	0.3	
2		150		11.20	7	2.8	-.60	98	58	0	9.0	4	0	38	38	20	58	12		
3	10	116		11.00	8	6.0	-.67	48	44	0										
4	15	120	.5	11.00	8	4.6	-.57	56	44	0	9.0	6	4	33	37	15	52	19	0	
5			10	7.55	8	2.6		0	0	66										
6			12	7.50	7	1.6		0	0	65	9.0	8	12	61	73	24	97			

Characteristics of raw water

Alkalinity as $CaCO_3$ 71

Total Hardness as $CaCO_3$ 86

pH. 7.60

Organic Color 8

Turbidity 7.5

Type Clay . . . . . . Natural

Magnesium as $CaCO_3$ 17

Comments

TABLE 33

$MgCO_3$ AND ALUM COAGULATION OF OPELIKA, ALABAMA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	5	90	.5	10.95	7	13	-.81													
2	10	92	.5	11.10	1	16	-.68	66	32	0								10		
3	20	106	0	11.10	2	12.5	-.49													
4	25	109	.5	11.15	3	3.4	+.43	72	32	0	9.0									
5			7	6.90	7	1.0														
6			10	6.80	4	0		0	0	14	9.0		3	18	21	9	30			

Characteristics of raw water		Comments
Alkalinity as $CaCO_3$	17	
Total Hardness as $CaCO_3$	17	
pH.	6.95	
Organic Color	10	
Turbidity	14	
Type Clay	Natural	

TABLE 34

LIME, $MgCO_3$, AND ALUM COAGULATION OF PHILADELPHIA, PENNSYLVANIA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1		120	.5	11.15	10	2.6	0	86	76	0	9.0	7	0	34	34	34	68	10		
2		135	.5	11.25	10	1.4	0	106	68	0	9.0	5	0	35	35	31	66	7		
3	10	133	.5	11.13	6	2.6	+.36	94	80	0	9.0	5	0	34	34	32	66	13		
*4		60		10.75	6	0.4		36	62	0	9.0		0	48	48	39	87	18		
5			15	7.10	9	1.8		0	0	30										
6			20	7.05	7	1.0		0	0	28	9.0	5	0	56	56	39	95	24		

Characteristics of raw water

Alkalinity as $CaCO_3$ 34
Total Hardness as $CaCO_3$ 69
pH. 7.40
Organic Color 14
Turbidity 41
Type Clay . . . . . . Natural
Magnesium as $CaCO_3$ 24

Comments

*2.0 mg/l $^{=}SiO_2^{=}$

TABLE 35

COAGULATION OF RICHMOND, VIRGINIA WATER WITH $MgCO_3$ AND ALUM

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	$MgCO_3$	$Ca(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	20	110	.5	11.25	23	14.0	0	78	52	0										
2	25	112	.5	11.25	16	5.8	+.34	80	54	0										
3	30	125	.5	11.30	12	2.6	+.43	98	50	0	9.0	5	0	40	40	15	55	15		
4	40	120	.5	11.25	9	2.8	+.62	86	56	0	9.0	5	0	38	38	15	53	17		
5		3	20	7.80	19	6	-	0	0	24	9.0	12	0	29	29	24	53			
6		3	23	7.70	12	2.6	-	0	0	22	9.0	8	0	31	31	24	55			

Characteristics of raw water	
Alkalinity as $CaCO_3$	27
Total Hardness as $CaCO_3$	43
pH.	7.90
Organic Color	30
Turbidity	24
Type Clay	Natural
Magnesium as $CaCO_3$	7

Comments

TABLE 36

$MgCO_3$ AND ALUM COAGULATION OF TUSCALOOSA, ALABAMA WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
1	15	83	.5	11.05	19	2.6	-.87													
2	20	86	.5	11.10	16	2.0	-.76													
3	20	97	.5	11.20	12	0.6	-.37													
4	25	100	.5	11.25	8	0.5	-.39	95	32	0	9.0		2	38	40	2	42	12		
5	--	1	7	6.70	7	.1	-.43	.0	0	.3	9.0		3	6	9	6	15			
6	--	2	10	7.00	9	.1	0													

Characteristics of raw water

Alkalinity as $CaCO_3$	4.0
Total Hardness as $CaCO_3$	5.0
pH.	6.3
Organic Color	26
Turbidity	4
Type Clay	Natural

Comments

TABLE 37

$MgCO_3$, LIME, AND ALUM COAGULATION OF WASHINGTON, D.C. WATER

Jar No.	Dosage in ppm			pH	Color	Turbidity	Mobility	Alkalinity			Stab. to pH	Color	Alkalinity		Hardness			Magnesium as $CaCO_3$		
	Mg CO_3	Ca $(OH)_2$	Alum					OH	CO_3	HCO_3			CO_3	HCO_3	C	NC	T			
*1		120		11.10	12	3.0	0	76	48	0										
*2	10	127		11.10	8	2.2	+.49	78	48	0										
3	15	130	.5	11.10	7	2.0	+.41	72	54	0										
4	20	117	.5	10.95	11	2.6	+.72	56	64	0	9.0	5	4	44	48	27	75	18		
5			15	7.45	10	3.0		0	0	37										
6			20	7.40	6	1.5		0	0	33	8.4	7	0	40	40	36	76	17		

Characteristics of raw water

Alkalinity as $CaCO_3$ 41

Total Hardness as $CaCO_3$ 71

pH. 7.50

Organic Color 15

Turbidity 50

Type Clay . . . . . . Natural

Magnesium as $CaCO_3$ 17

Comments

Mobility of raw water -.96

*.5 mg/1 Hal96

TABLE 38

CALCULATED POTENTIAL PRODUCTION OF $MgCO_3 . 3H_2O$ BY 20 AMERICAN CITIES, 1968

City	M.g. Water treated daily	Mg^{++} in untreated water, ppm	Amount removed ppm	Annual production of $MgCO_3 . 3H_2O$ tons	Annual gross revenue at 2¢ per lb.
Indianapolis	80	22	18	12,500	$ 500,000
Des Moines	30	33	29	7,200	288,000
Kansas City, Mo.	98	18	14	11,800	472,000
Kansas City, Kan.	32	21	17	4,500	180,000
Flint, Mich.	36	25	21	6,400	256,000
Lansing, Mich.	x23	33	23	4,500	180,000
Minneapolis	70	13	9	5,000	200,000
St. Paul	46	14	10	3,800	152,000
St. Louis	190	14	10	16,400	656,000
Omaha	68	23	19	11,000	440,000
Cincinnati	112	10	6	5,800	232,000
Columbus	38	28	24	7,900	316,000
Oklahoma City	*15	*31	*27	3,300	132,000
Fort Wayne, Ind.	x25	20	16	3,300	132,000
Dayton, Ohio	70	33	24	14,500	680,000
San Diego	x50	29	25	10,400	416,000
St. Louis Co. W.C.	60	17	13	6,800	136,000
Austin, Tex.	x35	19	15	4,500	180,000
New Orleans	x120	11	7	7,200	288,000
Wichita, Kan.	35	14	10	3,000	120,000
				149,800	$5,956,000

TABLE 38 (Continued)

Comments

1967-1968

Morse plant 54 mgd Mg^{++} 15 - 4 = 11   11 x 54 = 594
Dublin plant 38 mgd Mg^{++} 28 - 4 = 24   38 x 24 = 912
Both plants 92 mgd Mg^{++} 20 - 8 = 12   92 x 12 = 1104
Preferred method would probably recover at Dublin only, and calculated on this basis.

*Oklahoma City has three treatment plants
Lake Overholzer - 6 mgd Mg^{++} = 29
Lake Hefner -15 mgd Mg^{++} = 31
Lake Draper -18 mgd Mg^{++} = 4

So calculations based on recovery at Hefner plant only.

St. Louis County Water Co. has four plants, 3 deriving water from the Missouri River, one from the Minimac River.
Calculation based on largest plant only.

ˣExtrapolated from 1962 data.

TABLE 39

CALCULATIONS OF POTENTIAL CONSUMPTION OF $MgCO_3 . 3H_2O$ BY WATER TREATMENT PLANTS IN THE UNITED STATES*

460 Plants	Serving	55,757.215	People	Use	Alum
70 Plants	Serving	11,282.820	People	Use	Iron Salts
530 Plants	Serving	67,040.035	People	Use	Al or Fe

(67×10^6) people x (55×10^3) gal. yr. = 3.7×10^{12} gal/yr.

3.700,000,000,000 gal. = 3,700,000 mg/yr.

25 ppm $MgCO_3 . 3H_2O$ = 200 lbs/mg.

15% make up = 30 lbs/mg.

3,700,000 x 30 = 111,000,000 lbs.

$$\frac{111{,}000{,}000 \text{ lbs.}}{2000} = 55{,}000 \text{ tons/yr.}$$

3400 filtration plants below 4 mgd (25,000 people)

25%	Treat	3 mgd	= 2600 mgd
25%	Treat	2 mgd	= 1700 mgd
50%	Treat	1 mgd	= 1700 mgd
	Total		6,000 mgd

6,000 mgd x 20 lbs/mg x 365 days = 43,800,000 lbs.

$$\frac{43{,}800{,}000 \text{ lbs.}}{2000} = 22{,}000 \text{ tons/yr.}$$

Total of all plants 77,000 tons/yr. 1963 basis

Corrected for 1971 production - 102,000 tons/yr.

*From 1964 USPHS summary of municipal water facilities in Communities of 25,000 or more.

*U.S. GOVERNMENT PRINTING OFFICE: 1972-484-483/101

1 *Accession Number*

W

2 *Subject Field & Group*

05D

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 *Organization*

Department of Public Utilities, City of Gainsville, P.O. Box 490,
Gainsville, Florida

6 *Title*

Magnesium Carbonate, A Recycled Coagulant for Water Treatment

10 *Author(s)*

Dr. A. P. Black
Dr. C. G. Thompson

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22 *Citation*

23 *Descriptors (Starred First)*

Water Purification, Coagulation, Chemical Precipitation, Sludge Treatment, Industrial Wastes.

25 *Identifiers (Starred First)*

27 *Abstract*

An entirely new system of water treatment has been developed. It is a unique combination of softening and conventional coagulation, and may be used for all types of waters, surface or ground, hard or soft. Magnesium carbonate is used as the coagulant and lime is added to precipitate gelatinous $Mg(OH)_2$, which is as effective as alum for the removal of both turbidity and organic color. The flocs formed are larger and heavier than alum floc, since they are "loaded" with $CaCO_3$. The sludge, composed of a slurry of $CaCO_3$, $Mg(OH)_2$ and clay is carbonated with CO_2 and the $Mg(HO)_2$ selectively and completely dissolved as the bicarbonate. The carbonated slurry is filtered and the filtrate recycled to the point of addition of chemicals to the raw water and reprecipitated with lime thus recovering both the coagulant and the sludge water. In small plants, the filter cake of $CaCO_3$ can be used as land fill. In larger plants, it is slurried in a flotation cell and the clay separated and used as land fill. The purified $CaCO_3$ is filtered and the cake passes to a multiple hearth furnace or Kiln and calcined to high quality lime. Chemical treatment costs are substantially reduced for most waters and the quality of the treated water is superior to that treated with alum.

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